Rotaxanated Polymers:

I. Synthesis and Purification of Cyclic Polydimethylsiloxane

II. Synthesis of Poly[(octene-*pseudorotaxa*-(α-cyclodextrin)]

A Dissertation
Presented to
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By

Bryan M. White

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Approved by:

Dr. Haskell Beckham, Advisor

Dr. David Collard

Dr. Pete Ludovice

Dr. Andrew Lyon

Dr. Laren M. Tolbert

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Date Approved

DEDICATION

To my grandparents, parents, and wife for instilling in me the importance of a Christ-centered life.

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LIST OF ABBREVIATIONS

30c10	30-crown-10
18c6	18-crown-6
α-CD	alpha-Cyclodextrin
ADMET	Acyclic diene metathesis
AIBN	Azobisisobutyronitrile
CH_2Cl_2	Methylene chloride
D_4	Octamethyltetracyclosiloxane
D_5	Decamethylpentacyclosiloxane
daBG	Diazo-blocking group
DSC	Differential scanning calorimetry
DDPE	1,3-bis(1-phenylethylenyl)benzene
ecPO	End-capped PO
EtOH	Ethanol
[F]-18c6	Perfluoro-18-crown-6
[F]-30c10	Perfluoro-30-crown-10
GC	Gas chromatography
GPC	Gel permeation chromatography
IC	Inclusion complex
IR	Infrared spectroscopy
LCCC	Liquid chromatography at the critical condition
MALDI-TOF MS	Matrix-assisted laser desorption/ ionization time-of-flight mass spectrometry
mvBG	Monovinyl blocking group
NMR	Nuclear magnetic resonance
PCL	Poly(ε-caprolactone)
PDMS	Poly(dimethylsiloxane)
PEG	Polyethylene glycol
PEO	Polyethylene oxide
PLLA	Poly($_L$-lactic acid)
PMA	Poly(methyl acrylate)
PMMA	Poly(methyl methacrylate)
PO	Polyoctene
PS	polystyrene
t-BuOH	*tert*-Butanol
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
WAXD	Wide-angle X-ray diffraction

SUMMARY

Polyrotaxanes possess a molecular architecture resembling that of a wheel and axle: linear polymer chains are threaded by cyclic molecules with no covalent bonds linking the two species. One of two methods can be employed for the preparation of polyrotaxanes: a template method to guide threading or an *in situ* polymerization of monomers in the presence of cyclic molecules. The research described in this dissertation was divided into two distinct sections, which were devoted to each method of polyrotaxane preparation, but the overall goal was to better understand these unique polymer systems.

The first step of synthesizing polyrotaxanes via the *in situ* polymerization method was to prepare a cyclic molecule. α,ω-Dihydroxy-PDMS was cyclized in the presence of base and a coupling agent in dilute solution, but the crude product also contained linear chains as well. In solution these chains were uncyclized, yet anionically charged, so a macroporous anion-exchange resin was added to remove these linear impurities. This was the first purification method that separated linear and cyclic molecules based strictly on their chemical differences.

Three sizes of α,ω-dihydroxy-PDMS (M_n~2,460, 4,200, and 6,000 g/mol) were subjected to similar conditions for cyclization, but the cyclic PDMS (n = 16 repeat units) was formed preferentially. A hypothesis that backbiting of the linear PDMS chain was occurring under these basic conditions was verified when cycles were prepared without adding the coupling agent to the solution. Attempts to thread cyclic PDMS (n = 16 repeat

units) indicated that the cycles adopted a globular structure in solution such that neither solvent nor polymer molecules were able to enter the cavity.

The second part of this dissertation included examining polyrotaxanes created by the template-directed threading of α-CD onto polyoctene. In recent years, hundreds of publications have described polyrotaxanes of cyclodextrin molecules threaded onto a variety of backbones. Little work has been published, though, regarding verification of the threaded molecules. Therefore, end-capped PO was synthesized from 1,9-decadiene and a monovinyl bulky compound by ADMET, which is a step-growth polymerization of an α,ω-diene. The addition of the monovinyl species to the reaction solution capped all of the PO chains with bulky groups to prevent threading of α-CD. PO and ecPO each were sonicated in aqueous solutions of α-CD; PO formed a white precipitate indicative of a rotaxanated polymer, but no precipitate formed by the addition of ecPO. These results provided evidence that PO had been included within the cavity of α-CD.

Solvent effects on the formation of a precipitate from α-CD solutions were also examined. A solution of ecPO in THF was mixed with a solution of α-CD in water, and a white crystalline precipitate formed. However, the crystals dissolved after being washed repeatedly with THF and water, which suggested no rotaxane was prepared despite the precipitation of a white solid from solution. Therefore, THF was charged to an aqueous solution of α-CD, and the precipitate was examined. Current techniques available to characterize complexes of α-CD, such as ^{13}C CP/MAS NMR and WAXD, were unable to distinguish differences in the α-CD molecules that were threaded onto polymer chains versus α-CD molecules complexed with solvent.

I. Synthesis and Purification of Cyclic PDMS

CHAPTER 1

INTRODUCTION

1.1 ROTAXANATED POLYMERS VIA STATISTICAL THREADING METHODS

Rotaxanated polymers, catenanes, and interpenetrating networks comprise a unique class of macromolecules that incorporate two molecules through physical, instead of chemical, linkages. As shown in Figure 1.1, the molecular architecture of polyrotaxanes resembles that of a wheel and axle, such that a linear polymer penetrates the cavity of a cyclic species.[1,2] True polyrotaxanes require cyclic molecules to be threaded onto polymer segments that contain bulky end groups to block dethreading of the cyclic component, while polypseudorotaxanes lack these blocking groups. When both types of polymer systems are discussed without a distinction between the two, the phrase *rotaxanated polymers* is used.[3]

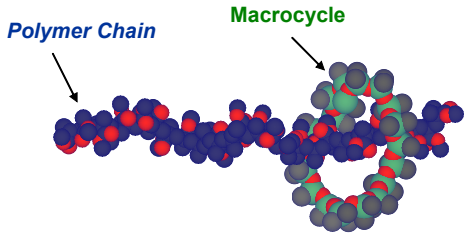


Figure 1.1 – Cartoon representing a linear polymer chain threaded by a cyclic molecule to form a polyrotaxane.

Rotaxanated polymers represent a flexible means of enhancing polymer properties. When the cyclic components and linear polymers onto which they are threaded have different chemical structures, the assemblies are particularly promising for applications which require the permanent combination of properties from two different types of materials. For example, coatings formulations often employ a base polymer to provide adhesion to the substrate and mechanical strength, while the topcoat exhibits the chemical functionality needed at the surface.[4-6] In this scenario, polyrotaxanes are proposed as a method of supplying the base polymer with the desired bulk properties threaded by a cyclic species which segregates to the surface (see Figure 1.2).

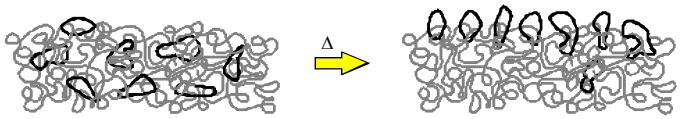


Figure 1.2 – Schematic of an as-cast film of a heterogeneous rotaxanated polymer (left) and the thermal-annealing-induced macrocycle segregation to the film surface (right). This concept is proposed as a flexible method for creating polymeric coatings with chemically different surfaces (e.g., fluorinated or siloxanated) from the bulk material.

Two approaches are available toward the synthesis of polyrotaxanes: (1) a template method which directs the threading of cyclic onto linear components and (2) *in situ* polymerization of monomers in the presence of the macrocycles. The most versatile means of creating rotaxanated polymers is by this *in situ* polymerization, but no thermodynamic driving forces for threading are present.[7,8]

The most common method of polyrotaxane formation utilizes thermodynamic interactions to promote threading. One such example is the threading of cyclodextrin onto poly(ethylene glycol) (PEG); under aqueous conditions, the hydrophobic core of

cyclodextrin provides a favorable nonpolar environment for PEG.[9,10] Another example includes threading crown ethers onto preformed polyurethane, where hydrogen bonding encourages interactions between the ether and amino groups, respectively.[11] Though this method of rotaxanation is more efficient and generally leads to higher threading ratios (i.e. number of cyclic components divided by the number-average number of repeat units), this method lacks versatility. The more general technique for incorporating polymers of varying species into the same system utilizes macrocycles as solvent during the polymerization, which allows for the preparation of a variety of rotaxanes with various backbones and macrocycles. The major drawback, of course, is that no driving force is present to promote threading, so low threading ratios are expected.[2]

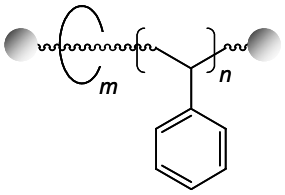
Polymer blends possess the benefit of incorporating two or more polymers with the desired properties into a single system, but macrophase segregation or polymer leaching are drawbacks that make the system less effective. Research employing block and graft copolymers attempt to overcome these issues. For example, a polymer backbone can provide the mechanical properties desired, while the grafted side chains modify the surface of the polymer film.[12] But as one may imagine, the chemistry associated with grafting onto various polymer backbones differs with each polymer; grafting onto poly(styrene) (PS) requires quite different chemistry than grafting onto poly(methyl methacrylate) (PMMA). Polyrotaxanes offer the opportunity to overcome both major issues associated with blend and graft copolymers: (1) properties of two polymers can be combined without concerns of macrophase segregation or leaching because the components are physically linked to one another and (2) polyrotaxanes can be formed simply by altering the polymer formulation by the addition of macrocycles,

which become physically trapped onto the polymer backbone. Another benefit is the mobility of the macrocyles, which are capable of moving along the linear chain and circumferentially as well.

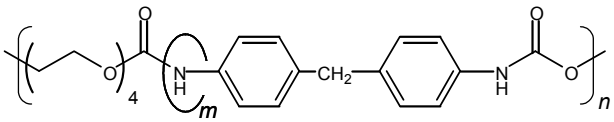
Little research has been done in regards to *in situ* threading of macrocycles onto linear polymer backbones when absolutely no driving forces for threading are present; only three examples, poly(styrene-*rotaxa*-crown ethers),[8] poly(methyl methacrylate-*rotaxa*-crown ethers),[13] and poly(methylacrylate-*rotaxa*-crown ethers),[13] have been reported. The formation of these systems is due to statistical mixing, and as a result, low threading yields were observed. Threading was observed to be a function of cavity area of the macrocycle relative to the cross sectional area of the linear backbones; therefore, larger rings yielded higher threading ratios.

Poly(urethane-*rotaxa*-crown ethers) have been synthesized through *in situ* experimental methods by polymerizing tetrakis(ethylene glycol) with bis(*p*-isocyanophenyl)methane through step-growth means utilizing crown ethers as the solvent, but this threading is driven by hydrogen-bonding forces between the crown ethers and amine groups as evidenced by the high threading ratios.[1] Poly(styrene-*rotaxa*-crown ethers) was synthesized by the free radical polymerization of styrene in the presence of crown ethers with toluene utilized as a cosolvent; these results are summarized in Figure 1.3. Though the threading ratios were low, some of the physical properties of PS were altered. The hydrophilic crown ethers caused PS to form emulsions in protic solvents such as water and methanol. The phenomenon was explained through a model that suggested a particle in solution with a PS-rich hydrophobic core and a crown ether-rich hydrophilic shell.[8] Thus, an example was shown

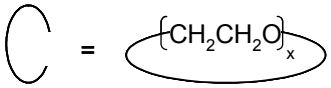
of the potential area of utilization for polyrotaxanes extending to simple property changes; the rotaxanated system showed surface active behavior due to the combination of two components with different solution properties.

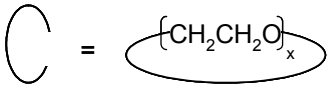


Poly(styrene-*rotaxa*-crown ether)



Poly(urethane-*rotaxa*-crown ether)





Ring Size (# atoms)	Threaded?	Mass % Cycles
18	No	-
30	Yes	1.4 %
34	Yes	3.5 %
36	n/a	n/a
42	Yes	21.0 %
48	n/a	n/a
60	n/a	n/a

Ring Size (# atoms)	Threaded?	Mass % Cycles
18	No	-
30	n/a	n/a
34	n/a	n/a
36	Yes	16.0 %
42	Yes	29.0 %
48	Yes	45.0 %
60	Yes	63.0 %

n/a = not attempted

Figure 1.3 – Results from threading PS by various sizes of crown ethers demonstrated that the amount of threading was directly related to the size of the ring. Polyurethane was threaded by various sizes of crown ethers and demonstrated this point as well, but threading was also encouraged by the hydrogen bonding affinity of the ether group toward the amino moiety.

1.2 PROPERTIES OF POLYDIMETHYLSILOXANE (PDMS)

Copolymer systems containing PDMS have been studied extensively because of the unique properties PDMS provides: a low glass transition temperature (T_g), low

surface energy, lubricity, thermal stability, and gas permeability.[14-18] These materials also reduce adhesion of biological organisms, and have shown to be physiologically inert and resistant to attack by biological systems.[19] Assimilating polysiloxane components, even in small amounts, into a polymer alters these material characteristics. The combination of properties instilled to a system by the addition of siloxanes has offered several opportunities for applications such as antifouling or fouling-release coatings in marine and physiological environments.[14,20-22]

Physical properties of siloxanes, especially PDMS, arise from the flexibility of the siloxane backbone induced by the long Si–O bond (1.64 Å *versus* 1.54 Å for C–C or 1.43 Å for C–O), the low Si–O torsional barrier, and the wide bond angles at the Si and O atoms that alternate between 110° and 142°.[23-25] This flexibility and mobility of the polymer backbone allows the nonpolar methyl groups to arrange in such a fashion that the lowest energy state may be easily maintained.[23,26] Thermal stability of these polymers is explained by the Si–O bond dissociation energy of 445 kJ/mol relative to 346 kJ/mol for C–C and 358 kJ/mol for C–O bonds, which arises from the partial ionic nature of the Si–O bond.[23,27]

Low-energy surfaces are achieved by the application of a small amount of PDMS. In cases where PDMS is applied as a blend or copolymer, annealing the polymer system allows the PDMS to migrate to the surface of the material. With the siloxane at the surface of the material, physical properties of the bulk polymer remain virtually unchanged. Numerous reports utilizing techniques such as contact angle measurements and XPS to study polymer surfaces, have indicated that the presence of as little as 1-2% by weight of PDMS provides a surface completely covered by the siloxane.[14,28-39]

Segregation of a PDMS block copolymer also provides an opportunity to prepare a film with an excess of siloxane required to cover a surface, so that the PDMS within the bulk can act as a reservoir for renewal of the low energy surface after surface erosion has occurred.[12]

The driving force for this research is to synthesize and evaluate cyclic components, which may be incorporated into polyrotaxane polymer systems. Cyclic perfluorocarbon ethers are studied because of their unique surface energy properties.[16] Cyclic poly(dimethyl siloxane) (PDMS) is the primary macrocycle studied in this research because of its low surface energy, low T_g, ability to alter surface properties of hydrocarbon polymer systems in blends or copolymers, and its solubility in common organic solvents.

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CHAPTER 2

CHARACTERIZATION AND ATTEMPTED ROTAXANATION OF PERFLUORO-CROWN ETHERS

2.1 INTRODUCTION

Initial work toward the production of surface-modified polymer backbones was pursued utilizing perfluoro crown ethers. Fluorinated compounds have long been used for their low surface energy properties[1] (e.g., Teflon) and crown ethers have been reported as threaded onto polyester backbones simply by adding the crown ethers to the polymerization formulation.[2-8] With this in mind, perfluoro-30-crown-10 ([F]-30c10) was prepared and subjected to threading by poly(decamethylene sebacate).

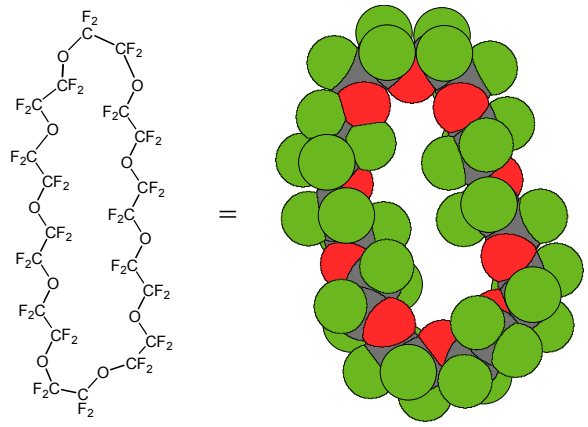

Figure 2.1 – Chemical structure and space-filling model of [F]-30c10.

A striking difference between the work previously reported regarding crown ethers and the current work involving their perfluorinated counterparts is the difference in attractive forces for threading. Crown ethers are inherently basic and the oxygen atoms

along the ring coordinate to cationic species. In this case, crown ethers hydrogen-bond to hydroxyl protons of the alcoholic monomers, which facilitates threading (see Figure 2.2). The crown ethers are given an opportunity to equilibrate with the monomers, then when polymerization is commenced, the crowns are trapped onto the polymer backbone.

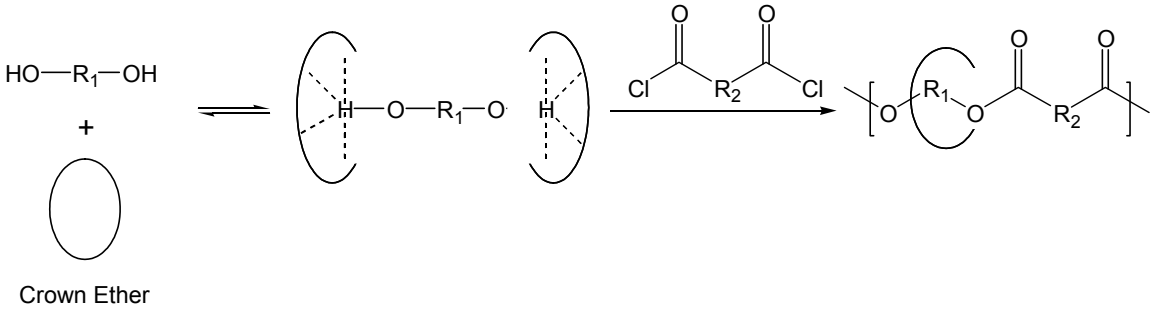

Figure 2.2 – Hydrogen bonding between the hydroxyl protons and crown ether oxygen atoms in the prethreading process.[3] The phenomenon does not occur between diols and perfluoro crown ethers because the fluorination diminishes the basicity of the oxygen atoms.

Perfluorinated versions of crown ethers do not have this same basicity. As a matter of fact, perfluoro-12-crown-4 ([F]-12c4), perfluoro-15-crown-5 ([F]-15c5), and perfluoro-18-crown-6 ([F]-18c6), have all been shown to be excellent carriers for O_2^- and F^-, but not with cations even though x-ray diffraction indicated that [F]-18c6 is puckered and the oxygen atoms are projected outward.[9] Further work into this matter suggested that the basicities of crown ethers decreased as the amount of electronegative fluorine substitution increased.[10] These data implied that no thermodynamic driving force was available to promote threading and that rotaxanation must occur entirely through statistical means. An advantage of perfluorinated crowns, though, was that the cycles were expected to maintain an open cavity, which was due to the higher C–C torsional

barrier. Substituting fluorine for the much smaller hydrogen atoms decreases chain flexibility and increases the rigidity of the cyclic backbone.

2.2 EXPERIMENTAL PROCEDURE

2.2.1 Materials

All reagents were used as received unless otherwise noted. Hexafluorobenzene (99.5%, NMR grade), trifluoroacetic acid (99%), perfluorohexanes (95%), 2,2,2-trifluoroethanol (99%), 2-chloro-2-difluoromethoxy-1,1,1-trifluoroethane (97%), 2-chloro-1-difluoromethoxy-1,1,2-trifluoroethane (97%), triphenylpropionic acid (97%), and methylene chloride (anhydrous, 99.8%) were purchased from Aldrich. 1,10-Decanediol (98%) was purchased from Aldrich and recrystallized from water and dichloroethane. Sebacoyl chloride (99%) was purchased from Aldrich and purified by vacuum distillation. 2-Chloro-1-ethoxy-1,1,2-trifluoroethane (97%) and 2-chloro-1,1,2-trifluoro-1-methoxyethane (97%) were purchased from Oakwood Chemical.

2.2.2 Instrumentation

IR spectroscopy was performed on a Bruker Vector 22. Liquid samples were analyzed on KBr salt plates and solid samples were analyzed by making pellets with KBr. GPC was conducted in THF (1 ml/min) at 303 K on three Waters Styragel columns (5 μm beads: HR 1, 100 Å, HR 3, 1000 Å, HR 4, 10,000 Å) that were connected to a Waters 2690 separations module and Waters 2410 refractive index detector. ^{1}H, ^{13}C and ^{19}F NMR spectra were measured on a Varian Gemini 300 at room temperature in C_6F_6 with

tetramethylsilane as an internal standard. Mass spectrometry was carried out on a VG Instruments 70SE in isobutane.

2.2.3 Synthesis

Glassware was dried at 120 °C overnight; all liquid transfers occurred via gastight syringes unless otherwise noted.

Polyrotaxanation Attempt with Freon113:CH_2Cl_2.

Into an oven-dried 25-ml, three-neck flask equipped with a stir bar, rubber septa, and a nitrogen inlet were added methylene chloride (1.0 ml) and Freon 113 (2.0 ml) via syringe followed by the addition of [F]-30c10 (1.0 ml, 0.86 mmol) and sebacoyl chloride (0.080 ml, 0.372 mmol) via syringe. Under constant nitrogen flow, 1,10-decanediol (0.0649 g, 0.372 mmol) and 3,3,3-triphenylpropionic acid (0.00056 g, 0.001 mmol) were added by spatula. The mixture was heated to 30 °C to promote dissolution and stirred overnight. After ~18 hrs, the solution had become cloudy. The reaction was cooled to room temperature, and the precipitate was filtered. Polymer was dried under vacuum and analyzed by ^{1}H, ^{13}C, and ^{19}F NMR.

Polyrotaxanation Attempt with 2-chloro-1,1,2-trifluoro-1-methoxyethane:CH_2Cl_2.

Into an oven-dried 25-ml, three-neck flask equipped with a stir bar, rubber septa, and a nitrogen inlet were added methylene chloride (1.0 ml) and 2-chloro-1,1,2-trifluoro-1-methoxyethane (1.0 ml) via syringe followed by the addition of [F]-30c10 (1.0 ml, 0.86 mmol) and sebacoyl chloride (0.080 ml, 0.372 mmol) via syringe. Under constant

nitrogen flow, 1,10-decanediol (0.0712 g, 0.372 mmol) and 3,3,3-triphenylpropionic acid (0.00062 g, 0.001 mmol) were added by spatula. The mixture was heated to 30 °C to promote dissolution and stirred overnight. After ~18 hrs, the solution had become cloudy. The reaction was cooled to room temperature, and the precipitate was filtered. Polymer was dried under vacuum and analyzed by ^{1}H, ^{13}C, and ^{19}F NMR.

Polyrotaxanation Attempt with 2-chloro-1-difluoromethoxy-1,1,2-trifluoroethane:CH_2Cl_2.

Into an oven-dried 25-ml, three-neck flask equipped with a stir bar, rubber septa, and a nitrogen inlet were added methylene chloride (1.0 ml) and 2-chloro-1-difluoromethoxy-1,1,2-trifluoroethane (2.0 ml) via syringe followed by the addition of [F]-30c10 (1.0 ml, 0.86 mmol) and sebacoyl chloride (0.080 ml, 0.372 mmol) via syringe. Under constant nitrogen flow, 1,10-decanediol (0.0695 g, 0.372 mmol) and 3,3,3-triphenylpropionic acid (0.00061 g, 0.001 mmol) were added by spatula. The mixture was heated to 30 °C to promote dissolution and stirred overnight. After ~18 hrs, the solution had become cloudy. The reaction was cooled to room temperature, and the precipitate was filtered. Polymer was dried under vacuum and analyzed by ^{1}H, ^{13}C, and ^{19}F NMR.

2.3 RESULTS AND DISCUSSION

2.3.1 Characterization of Perfluorinated Crown Ethers

[F]-18c6 and [F]-30c10 were synthesized from their hydrogenated precursors. 18cr6 was used as received from Aldrich, but 30c10 was prepared by Stephanie Dilocker according to a literature procedure.[11] Pentaethylene glycol was deprotonated by sodium

hydride and reacted with ditosylated-pentaethylene glycol under dilute solution conditions in THF to yield 30c10 in ~30% yield, which was purified by repeated fractional precipitations. Pure 30c10 and 18c6 were perfluorinated by George Moore and Jay Schulz at 3M by subjecting the hydrogenated material to 20% elemental fluorine under an inert atmosphere.[12]

The synthesis of [F]-18c6 had previously been reported, and the mass spectrum was described in detail.[9,13,14] Results from the work contained herein indicated that [F]-18c6 had indeed been synthesized. The mass spectrum of [F]-18c6 was well resolved and almost identical to that previously reported. An $[M+H]^+$ peak was observed at 697 amu, an $[M-F]^+$ peak was seen at 677 amu, and fragmentation occurred with losses of perfluoroethylene oxide repeat units. However, a mass spectrum for [F]-30c10 yielded only a base peak at 614 amu, which did not correspond to any known fragment.

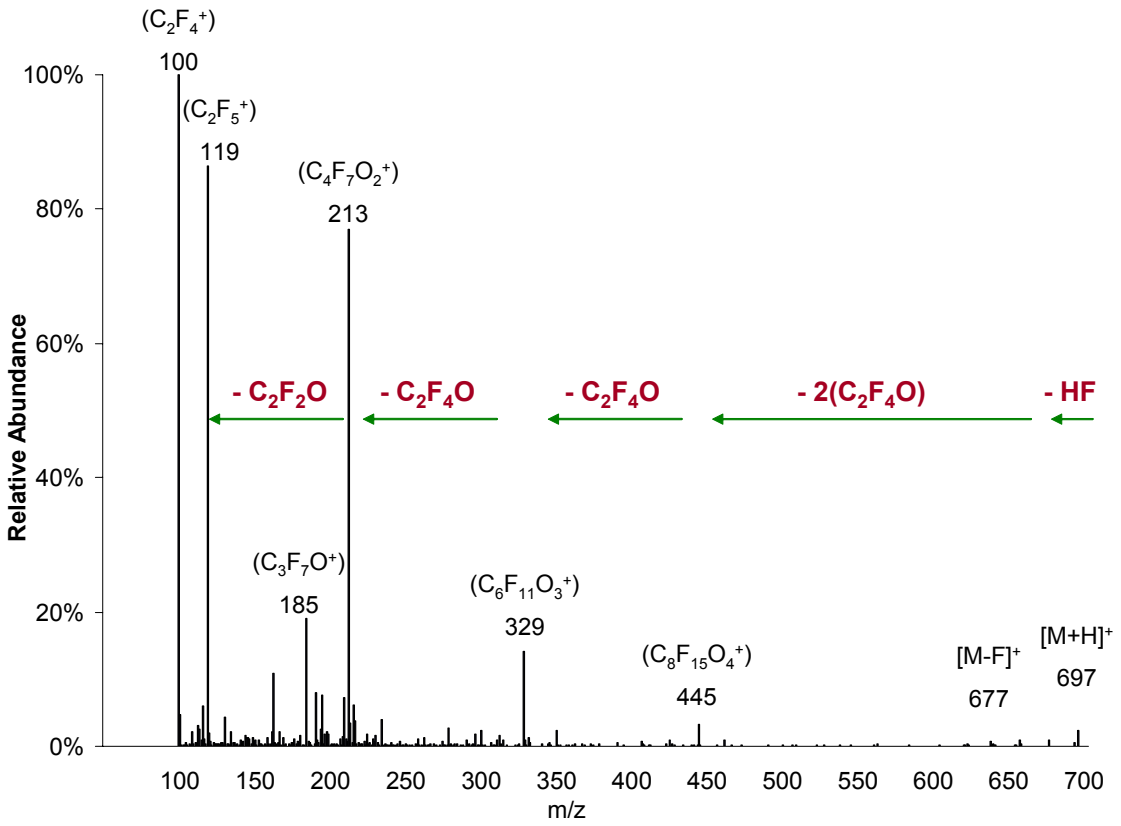

Figure 2.3 – Mass spectrum of [F]-18c6 demonstrating an $[M+H]^+$ peak at 697 amu, an $[M-F]^+$ peak at 677 amu, and fragmentation occurring with losses of perfluoroethylene oxide repeat units.

The perfluorinated crown ethers were further analyzed by NMR spectroscopy. ^{13}C NMR demonstrated a triplet of triplets for both [F]-18c6 (see Figure 2.4) and [F]-30c10 (see Figure 2.5) at 118.6 ppm and 113.3 ppm, respectively, relative to TMS with coupling values of $^1J_{C-F} = 285$ Hz and $^2J_{C-CF} = 45$ Hz. The samples were analyzed using a proton-decoupling pulse sequence, but since the protons had been replaced by fluorine, coupling between the fluorines attached to the carbon atoms along with splitting from the fluorines on the adjacent carbons was observed.

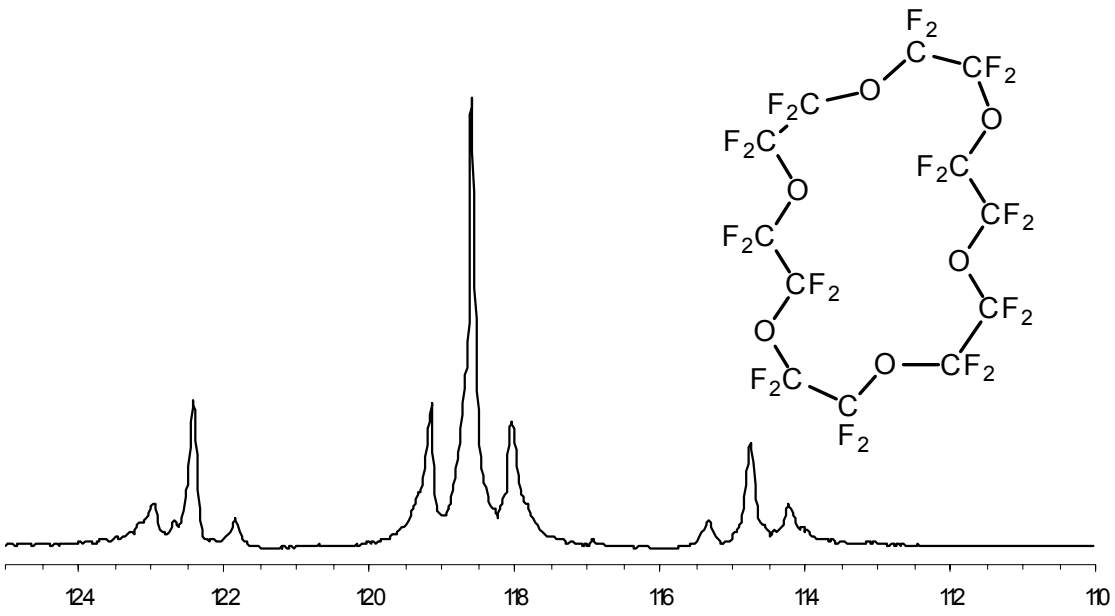

Figure 2.4 – ^{13}C NMR spectrum of [F]-18c6 demonstrating a triplet of triplets centered at 118.6 ppm relative to TMS with *J*-coupling values of $^{1}J_{C-F}$ = 285 Hz and $^{2}J_{C-CF}$ = 45 Hz.

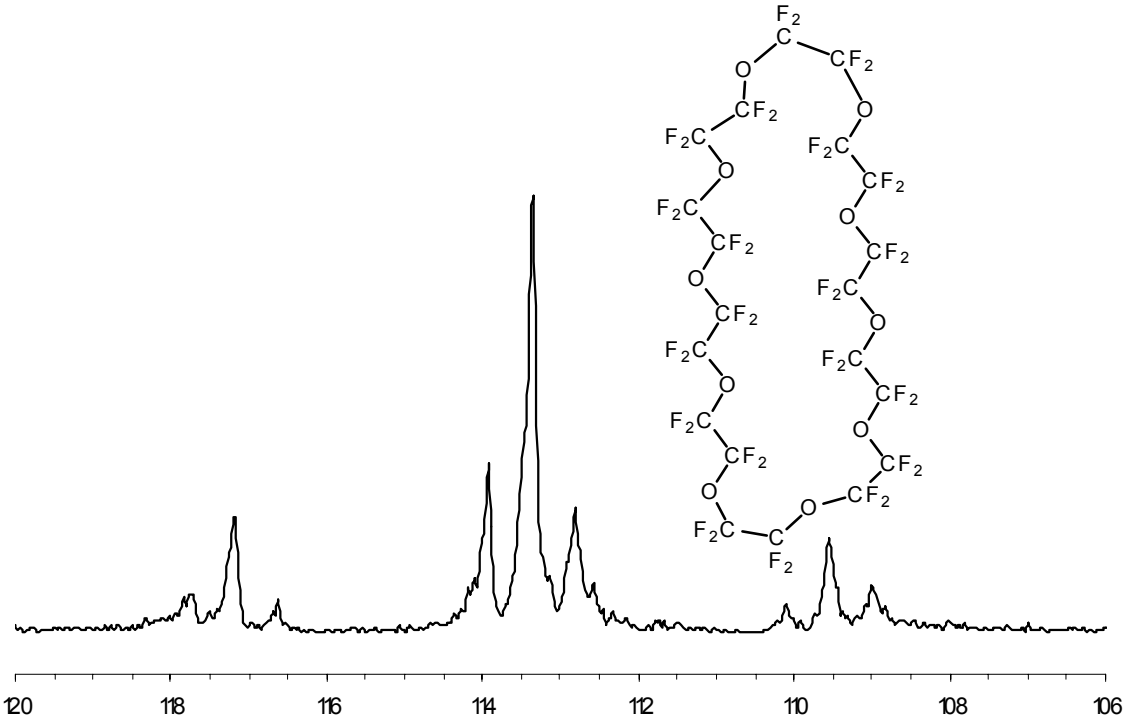

Figure 2.5 – ^{13}C NMR spectrum of [F]-30c10 demonstrating a triplet of triplets centered at 113.3 ppm relative to TMS with *J*-coupling values of $^{1}J_{C-F}$ = 285 Hz and $^{2}J_{C-CF}$ = 45 Hz.

A singlet was expected in the ^{19}F NMR for each perfluorinated crown in solution because each fluorine atom along the cycle is in a similar chemical environment. This in fact was observed: [F]-18c6, -86.0 ppm (actual) *versus* -91.0 ppm (lit.);[9] [F]-30c10, -89.0 ppm (actual) *versus* -89.5 ppm (lit.),[15] but smaller peaks were also present in each spectrum. This indicated that more than one molecule was present in the fluorinated mixture. Gas chromatography (GC) supported this conclusion and provided evidence that [F]-18c6 was present in ~80% yield while [F]-30c10 was present in ~70% yield. The impurities were formed during the harsh fluorination process, which can lead to chain scission and incomplete perfluorination.[9]

2.3.2 Attempted Rotaxanation onto Polyesters

Perfluoro-crown ethers were insoluble in common organic solvents, but were found to be soluble in a variety of fluorinated and chlorofluorinated solvents including hexafluorobenzene, trifluoroacetic acid, perfluorohexane, 2,2,2-trifluoroethanol, Freon 113, 2-chloro-2-difluoromethoxy-1,1,1-trifluoroethane, 2-chloro-1,1,2-trifluoro-1-methoxyethane, 2-chloro-1-difluoromethoxy-1,1,2-trifluoroethane, and 2-chloro-1-ethoxy-1,1,2-trifluoroethane. Unfortunately, none of these potential solvent candidates dissolved the esterification monomers, 1,10-decanediol and sebacoyl chloride, nor the end-capping agent, triphenylpropionic acid. Therefore, a co-solvent system was employed to combat this issue by combining methylene chloride (CH_2Cl_2), which was a good solvent for the monomers, with each of these halogenated solvents to dissolve all of the components necessary for rotaxanation.

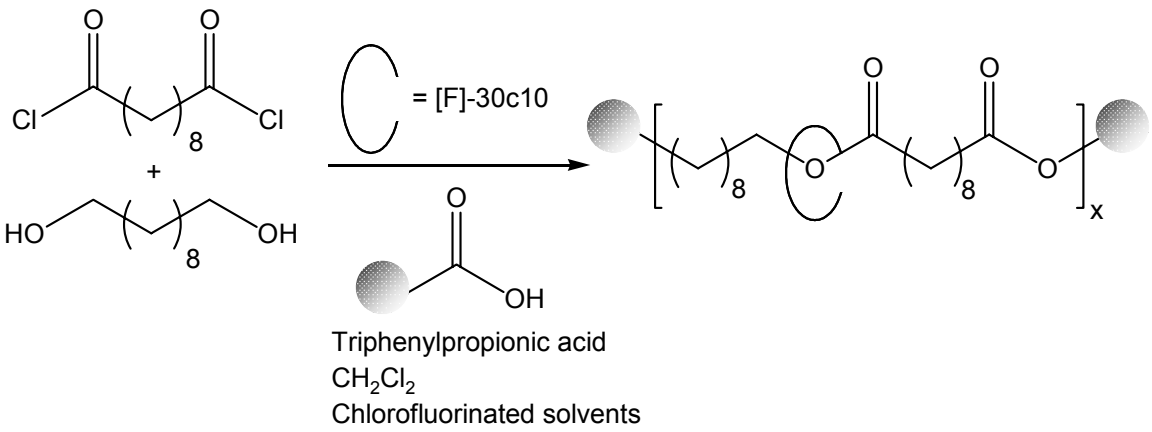

Figure 2.6 – Synthetic scheme for polymerizing 1,10-decanediol with sebacoyl chloride via esterification in the presence of [F]-30c10 by incorporating a ternary chlorofluorinated solvent with methylene chloride.

Solubility tests were performed to determine the best solvents and solvent ratios for esterification to occur in the presence of [F]-30c10; Freon 113:CH_2Cl_2 (2:1), 2-chloro-1,1,2-trifluoro-1-methoxyethane:CH_2Cl_2 (1:1), and 2-chloro-1-difluoromethoxy-1,1,2-trifluoroethane:CH_2Cl_2 (2:1), dissolved [F]-30c10, triphenylpropionic acid, and the monomers. A typical polymerization as shown in Figure 2.6 simply entailed dissolving the four components in the appropriate solvents and stirring overnight. Initially, a clear solution was observed, but as polymerization ensued, the clear solution became cloudy indicating that polymer precipitation had taken place. The polymer was filtered from solution, dried under vacuum, and analyzed by ^{13}C and ^{19}F NMR to determine whether or not [F]-30c10 had been trapped onto the polymer backbone. Unfortunately, no peaks were found to indicate the perfluorinated crown ether had been threaded.

2.4 CONCLUSIONS

[F]-18c6 and [F]-30c10 were synthesized from their hydrogenated precursors under harsh fluorinating conditions and characterized by mass spectrometry, ^{13}C NMR, ^{19}F NMR, and GC. The mass spectrum for [F]-18c6 was comparable to that previously reported and gave a clear indication that 18c6 had been perfluorinated as evidenced by the $[M+H]^+$ peak at 697 amu, the $[M-F]^+$ peak at 677 amu, and fragmentation occurring with losses of perfluoroethylene oxide repeat units. A mass spectrum for [F]-30c10 yielded only a base peak at 614 amu.

A ^{13}C NMR spectrum of [F]-18c6 exhibited a triplet of triplets centered at 118.6 ppm relative to TMS, while a ^{13}C NMR spectrum of [F]-30c10 described a triplet of triplets centered at 113.3 ppm. Both sets of peaks included *J*-coupling values of $^{1}J_{C-F}$ = 285 Hz and $^{2}J_{C-CF}$ = 45 Hz. A singlet was shown in the ^{19}F NMR for each perfluorinated crown in solution because each fluorine atom along the cycle was in a similar chemical environment, but smaller peaks were also present in each spectrum indicating that more than one molecule was present in the fluorinated mixture. GC supported this conclusion and suggested that [F]-18c6 was present in ~80% yield while [F]-30c10 was present in ~70% yield. The impurities were formed during the fluorination process.

Attempts to thread [F]-30c10 were made by utilizing a cosolvent system of methylene chloride with various chlorofluorinated and chlorofluoroether solvents. The monomers, 1,10-decanediol and sebacoyl chloride, the fluorinated ether, [F]-30c10, and the end-capping agent, 3,3,3-triphenylpropionic acid, were successfully dissolved in a single solution. However, as polymerization transpired, polymer precipitated from solution before threading occurred.

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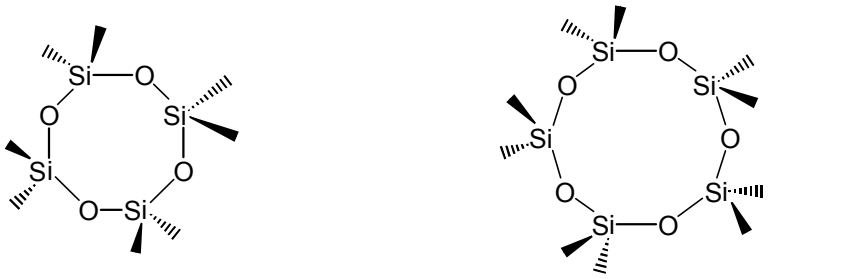
CHAPTER 3

SYNTHESIS AND PURIFICATION OF CYCLIC PDMS

3.1 INTRODUCTION

The synthesis of cyclic PDMS was first achieved through ring-chain equilibration of siloxane oligomers in the presence of potassium silanolate.[1-5] Octamethylcyclotetrasiloxane (D_4) and/or decamethylcyclopentasiloxane (D_5), which are exhibited in Figure 3.1, were heated in the presence of potassium hydroxide under neat conditions or refluxed in concentrated solutions of toluene. The subsequent polymerization with cyclic by-products was chain-stopped with trimethylchlorosilane, and fractionated by distillation (to remove D_3–D_6), solvent extraction, vapor phase chromatography, and gel permeation chromatography to yield milligram quantities of the individual cycles up to D_{225}.[3,4]



Octamethylcyclotetrasiloxane (D_4) Decamethylcyclopentasiloxane (D_5)

Figure 3.1 – Chemical structures of D_4 and D_5.

As pointed out by others,[6,7] the limitations of being restricted to low molar masses and the inability to directly compare the cyclic product with its linear counterpart, are overcome with a synthetic method based on the ring closure of α,ω-end-functionalized

linear polymers using a complementary difunctional coupling agent in dilute solution. This method has been successfully used to prepare cyclic poly(oxyethylene) (POE),[8-10] polystyrene (PS),[6,11] poly(2-vinylpyridine),[12] and PS-*block*-PDMS.[13]

Cyclic POE was synthesized in high yield (> 90%) by deprotonating hydroxyl-terminated linear POE with potassium hydroxide in a solution of methylene chloride, which also acted as the coupling agent to produce cyclic POE via an acetal linkage (Figure 3.2).[8-10]

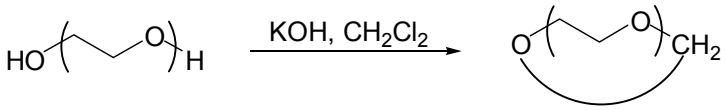


Figure 3.2 – Cyclization of hydroxyl-terminated POE through an acetal linkage by deprotonation with a strong base and coupling with methylene chloride.

Cyclic PS was prepared by polymerizing styrene with a dianionically-charged initiator, which was prepared from 1,3-bis(1-phenylethylenyl)benzene (DDPE) with two equivalents of *sec*-butyl lithium, and then coupling the charged, linear PS with DDPE under dilute conditions (see Figure 3.3). The desired product was separated from the chain extended PS by liquid chromatography at the critical condition (LCCC). This separation technique allows polymers to be separated by their heterogeneity, such as functional groups, graft copolymers, etc., by operating at the transition point between separation by size exclusion and separation by adsorption. At the critical point, all polymers of a particular topology elute at the same time whatever their molar mass allowing for the separation of cyclic polymers from their linear analogs. This technique required a critical point of adsorption to be determined by eluting PS standards on a silica gel stationary phase with a mixture of THF and n-hexane. The exclusion-adsorption

transition point occurs at the solvent composition where the retention time changes from increasing as a function of molecular weight to decreasing as a function of molecular weight. When retention time of the polymer increases as a function of molecular weight, the adsorption mode is in effect.[6]

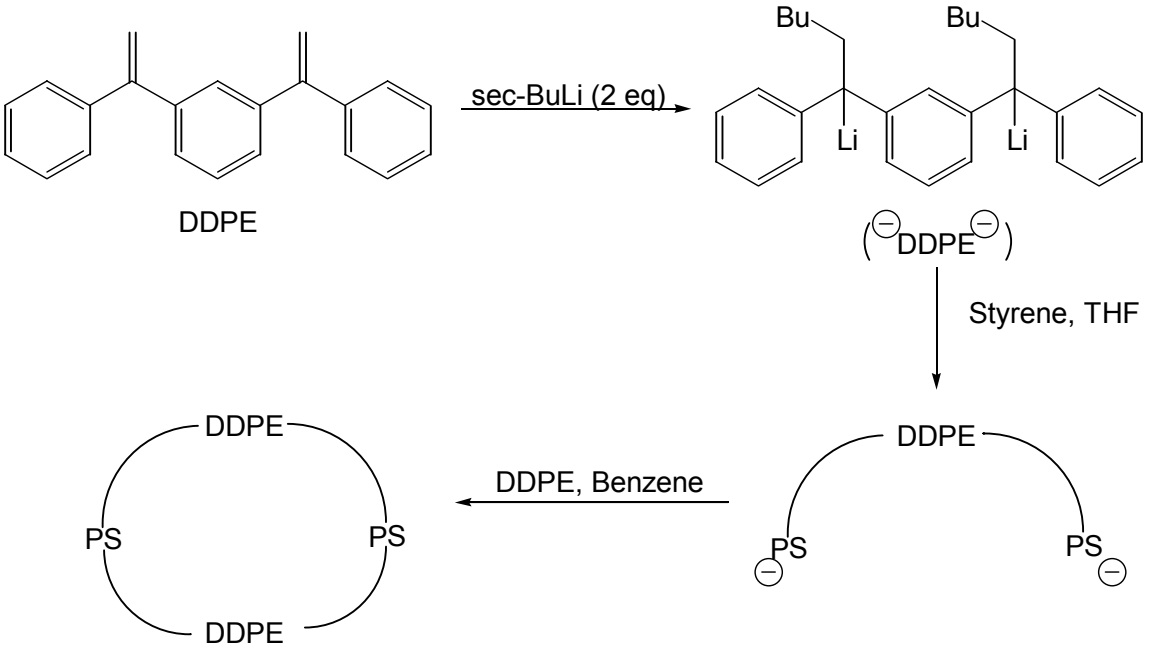


Figure 3.3 – Synthesis of cyclic polystyrene via coupling of a dianionically-charged linear PS chain with 1,3-bis(1-phenylethylenyl)benzene.

PS-*block*-PDMS was synthesized by initiating styrene with a difunctional initiator, lithium naphthalide, then adding D_3 to form a dianionically-charged triblock copolymer, PDMS–PS–PDMS. The reactive copolymer was then diluted in THF and cyclization occurred in the presence of the coupling agent, dichlorodimethylsilane. Cyclic PS-*block*-PDMS was separated from the unreacted linear precursors by fractional precipitation in THF/methanol.[13] This procedure was attempted in our lab using standard organic synthesis techniques and glassware. Difficulties arose with regards to

maintaining an atmosphere appropriate for anionic polymerization in dilute solution (i.e. completely proton and O_2 free) because glassware was not designed specifically for the synthesis of these cycles.

As shown in Figure 3.4, another method of cyclizing polymers includes initiating an anionic polymerization of a vinyl monomer with a functional initiator, which induces functionality at the α-position. The polymerization is then terminated with an agent that provides functionality in the ω-position, which is complimentary to the functionality introduced by initiation. Intramolecular end-to-end reactions occur by coupling of the two ends under a dilute solution environment. This method was undertaken by initiating the polymerization of styrene with 3-lithiopropionaldehyde diethyl acetal and terminating the reaction with successive additions of diphenyl ethylene and *p*-chloromethylstyrene, respectively.[14] In order for cyclization to occur, the α-acetal ends were reacted with trimethylsilyl iodide to provide the appropriate functionality to compliment the ω-vinyl end. A solution of α,ω-heterodifunctionalized PS in toluene was added dropwise to a large volume of toluene containing $SnCl_4$ to catalyze the reaction. Various lengths of PS (n = 14-60 repeat units) were cyclized. The cyclic PS was separated from chain-extended PS by fractionation and from unreacted linear precursors by LCCC.[15]

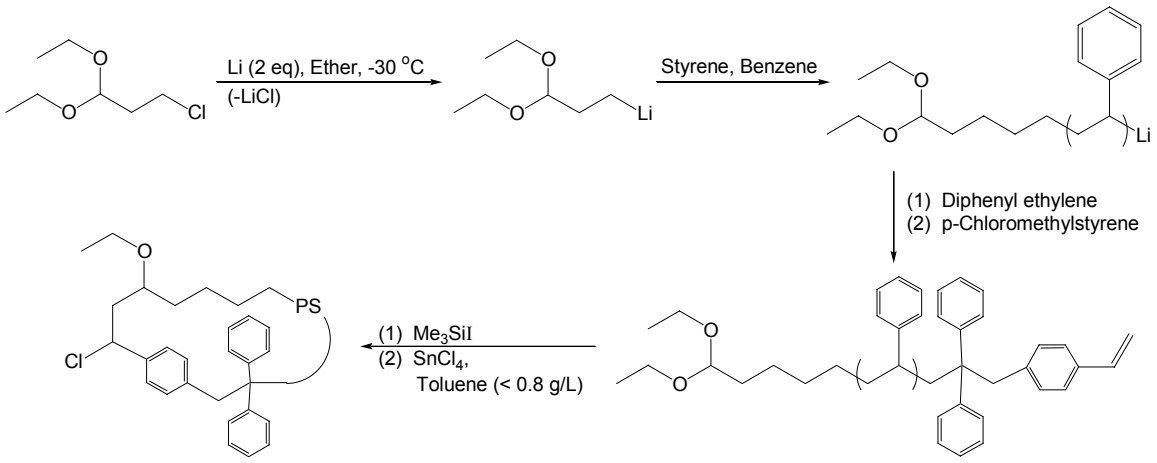


Figure 3.4 – Synthesis of α,ω-heterodifunctional linear PS and the cyclic product formed through an end-to-end coupling reaction of the complimentary end-groups under dilute solution.

These synthetic methods are successful in preparing various cyclic polymers, but major difficulties occurred with separating the desired cyclic material from the product mixture which still included linear byproducts from unreacted precursors, chain extension or end-capping of the linear precursor at one or both ends by the coupling agent. Methods such as fractional precipitation,[4] preparative GPC,[16] or LCCC[6,7,17] were utilized, but such purification steps typically reduced yields since the physical characteristics upon which they are based are similar for the cyclic polymers and their linear precursors. Tezuka has diminished the need for such purification steps by introducing a modification to the synthetic method in which the functional groups of both the polymer and coupling agent are charged.[18-20] Electrostatic self-assembly of the components is followed by covalent fixation to quantitatively yield a large variety of well-defined nonlinear polymer topologies. An example of this elegant method is demonstrated by the cyclization of PS as exhibited in Figure 3.5.[21]

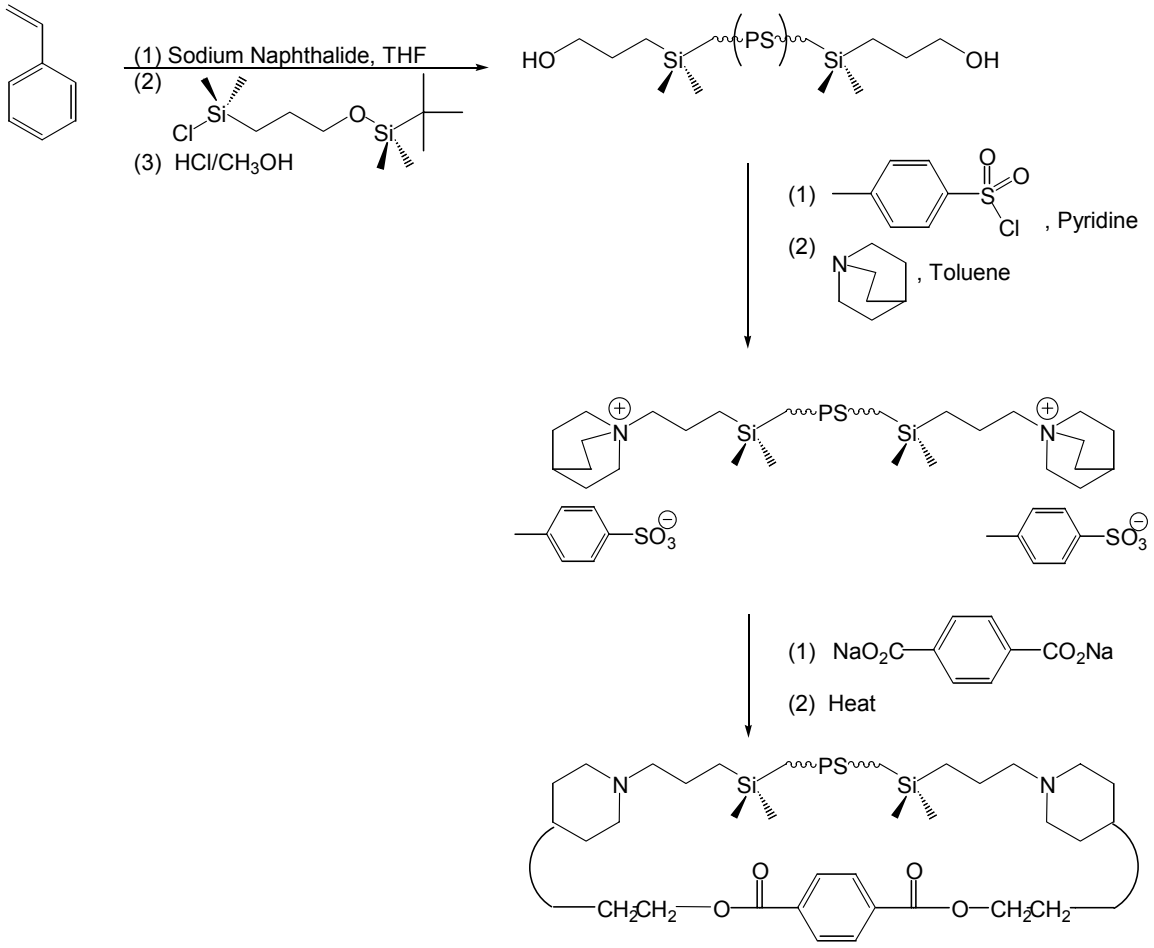


Figure 3.5 – Synthesis of cyclic polystyrene via electrostatic self-assembly in dilute solution.

While the Tezuka method is quantitative, the appropriate electrostatic functional groups must be incorporated onto the ends of the linear precursors. Similarly, appropriate complementary functional groups must be introduced at chain ends when using those methods based on the intramolecular end-to-end coupling of α,ω-heterodifunctional linear polymers.[22] On the other hand, commercially available α,ω-dihydroxy-functionalized polymers can be deprotonated, or vinyl monomers can be anionically polymerized to directly yield α,ω-dianion-functionalized polymers which are then cyclized simply by reaction with a difunctional electrophile. In this case, though, a

more efficient purification scheme is needed to remove the linear byproducts without decreasing the yields of cyclic polymer. The methods currently in use are based on physical properties; to completely remove linear byproducts from cyclic polymers using methods based on physical properties, portions of the cyclic material will be removed as well. Here we propose a modification to the synthetic method by which the two species may be effectively separated by their *chemical* differences. This is demonstrated for the synthesis of cyclic PDMS from commercially available α,ω-dihydroxy-PDMS. The linear precursor is deprotonated using sodium hydride in dilute THF ($\leq 10^{-2}$ *M*), and then a dichlorosilane agent was added for the purpose of end-coupling the anionically-charged ends. The uncyclized anionic linear precursors are then removed by a macroporous anion-exchange resin. The successful cyclization and purification is monitored by IR, ^{29}Si NMR, GPC, and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS).

3.2 EXPERIMENTAL PROCEDURE

3.2.1 Materials

All reagents were used as received. α,ω-Dihydroxy-PDMS (M_n~2,460 g/mol; M_n~4,200 g/mol) was purchased from Gelest. α,ω-Dihydroxy-PDMS (M_n~6,000 g/mol), sodium hydride (dry, 95%), dichlorodimethylsilane (99%), methanol (99%), tetrahydrofuran (anhydrous, 99.9%), and toluene (HPLC grade, 99.8%) were purchased from Aldrich. Macroporous anion-exchange resin AG MP-1M (1 meq/mL, 0.7 g/mL, 100-200 mesh, chloride form) was purchased from Bio-Rad Laboratories and dried under vacuum prior to use.

3.2.2 Instrumentation

GPC was conducted in toluene (1 mL/min) at 303 K on three Waters Styragel columns (5-μm beads: HR 1, 100 Å; HR 3, 1,000 Å; HR 4, 10,000 Å) that were connected to a Waters 2690 separations module and Waters 2410 refractive index detector. MALDI-TOF mass spectrometry was carried out on a Micromass TofSpec 2E with dithranol serving as the matrix and silver trifluoroacetate used for ionization. ^{1}H NMR were measured on a Varian Gemini 300 and Bruker AMX 400 in chloroform-d ($CDCl_3$). ^{29}Si NMR spectra were measured on a Bruker AMX 400 in chloroform-d ($CDCl_3$).

3.2.3 Synthesis

Cyclizations were conducted according to the procedures detailed below beginning with α,ω-dihydroxy-PDMS of three different molecular weights: M_n~2,460 g/mol, M_n~4,200 g/mol, and M_n~6,000 g/mol. In general, the following steps were taken to optimize reaction conditions: glassware was dried at 120 °C overnight, all liquid transfers occurred via gas-tight syringes unless otherwise noted, round-bottom flasks with stir bars were sealed with rubber septa and a stopcock adapter, and flasks were cooled while evacuating and then backfilling with dry N_2.

α,ω-Dihydroxy-PDMS (M_n~2,460 g/mol).

Into a 250-ml, 3-necked flask, THF (200 mL) was charged by cannula. Under positive nitrogen flow, a septum was removed and sodium hydride (0.0905 g, 3.8 mmol) was added. Immediately, α,ω-dihydroxy-PDMS (4.0 mL, 1.6 mmol based on the

number-average molecular weight) was added, and the mixture was stirred overnight followed by addition of a dilute solution of dichlorodimethylsilane (0.20 mL, 1.6 mmol) in THF (10 mL). The solution was stirred for another 24 hours before quenching with AG MP-1M anion-exchange resin (4.8 g). The mixture was stirred gently for four hours to ensure complete ion exchange before filtering. The solvent was removed by rotary evaporation, and the solid crude material was dissolved in toluene (200 mL), washed with distilled water (200 mL × 3) to remove salts, and dried over magnesium sulfate. The mixture was filtered and the solvent removed by rotary evaporation. Product was finally concentrated as a slightly viscous clear oil (3.03 g, 77% yield) by removing low-molecular-weight byproducts through vacuum distillation (T = 170 °C, P = 400 mTorr).

α,ω-Dihydroxy-PDMS (M_n~4,200 g/mol).

Into a 1-L, 3-necked flask, THF (800 mL) was charged by cannula. Under positive nitrogen flow, a septum was removed and sodium hydride (0.2479 g, 9.8 mmol) was added. Immediately, α,ω-dihydroxy-PDMS (20.0 mL, 4.7 mmol based on the number-average molecular weight) was added, and the mixture was stirred overnight followed by addition of a dilute solution of dichlorodimethylsilane (0.60 mL, 5.0 mmol) in THF (10 ml). The solution was stirred for another 24 hours before quenching with AG MP-1M anion-exchange resin (17.2 g). The mixture was stirred gently for four hours to ensure complete ion exchange before filtering. The solvent was removed by rotary evaporation, and the solid crude material was dissolved in toluene (200 mL), washed with distilled water (200 mL × 3) to remove salts, and dried over magnesium sulfate. The mixture was filtered and the solvent removed by rotary evaporation. Product was finally

concentrated as a slightly viscous clear oil (15.5 g, 79% yield) by removing low-molecular-weight byproducts through vacuum distillation (T = 170 °C, P = 400 mTorr).

α,ω-Dihydroxy-PDMS (M_n~6,000 g/mol).

Into a 1-L, 3-necked flask, THF (800 mL) was charged by cannula. Under positive nitrogen flow, a septum was removed and sodium hydride (0.1799 g, 7.5 mmol) was added. Immediately, α,ω-dihydroxy-PDMS (16.0 mL, 2.6 mmol based on the number-average molecular weight) was added, and the mixture was stirred overnight followed by addition of a dilute solution of dichlorodimethylsilane (0.55 mL, 4.0 mmol) in THF (10 mL). The solution was stirred for another 24 hours before quenching with AG MP-1M anion-exchange resin (8.87 g). The mixture was stirred gently for four hours to ensure complete ion exchange before filtering. The solvent was removed by rotary evaporation, and the solid crude material was dissolved in toluene (200 mL), washed with distilled water (200 mL × 3) to remove salts, and dried over magnesium sulfate. The mixture was filtered and the solvent removed by rotary evaporation. Product was finally concentrated as a slightly viscous clear oil (7.52 g, 48%) by removing low-molecular-weight byproducts through vacuum distillation (T = 170 °C, P = 400 mTorr).

α,ω-Dihydroxy-PDMS (M_n~2,460 g/mol) linear precursor with no coupling agent.

Into a 250-ml, 3-necked flask, THF (200 mL) was charged by cannula. Under positive nitrogen flow, a septum was removed and sodium hydride (0.0750 g, 3.12 mmol) was added. Immediately, α,ω-dihydroxy-PDMS (3.0 mL, 1.23 mmol based on the number-average molecular weight) was added, and the mixture was stirred for 96 hours.

The reaction was monitored by removing 20-30 ml of solution at various time intervals, quenching with methanol, removing the solvent via rotary evaporation, filtering to remove salts, and purifying the product by vacuum distillation (T = 170 °C, P = 400 mTorr).

Resin Regeneration.

Upon collection of the spent resin in a funnel, 100 mL of THF was poured into the funnel and allowed to flow under the influence of gravity only. When the liquid level approached the resin surface, 200 mL of 1 *M* HCl in THF was poured over the soaked resin and allowed to flow under the influence of gravity only. The resin was then washed with copious amounts of THF to remove traces of HCl.

3.3 RESULTS AND DISCUSSION

3.3.1 Cyclization beginning with α,ω-Dihydroxy-PDMS (M_n~2,460 g/mol)

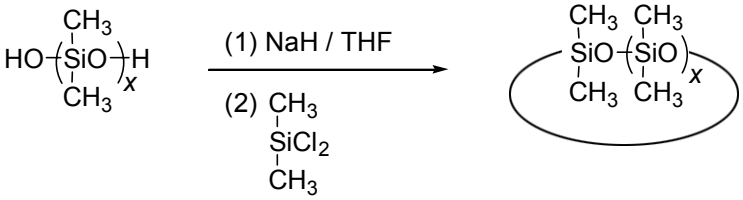


Figure 3.6 – Synthetic scheme for cyclization of linear α,ω-dihydroxy-PDMS.

Dihydroxy-terminated linear PDMS was converted to the corresponding silanolate-terminated species and then dichlorodimethylsilane was added as a coupling agent (see Figure 3.6). Chain cyclization was promoted over chain extension by conducting the reaction in dilute solution ($\leq 10^{-2}$ M). The reaction was followed by the disappearance of the hydroxy end groups with IR spectroscopy. In Figure 3.7 the IR spectrum of the linear PDMS revealed a broad –OH peak from 3120 to 3470 cm^{-1} that was not present in the product.

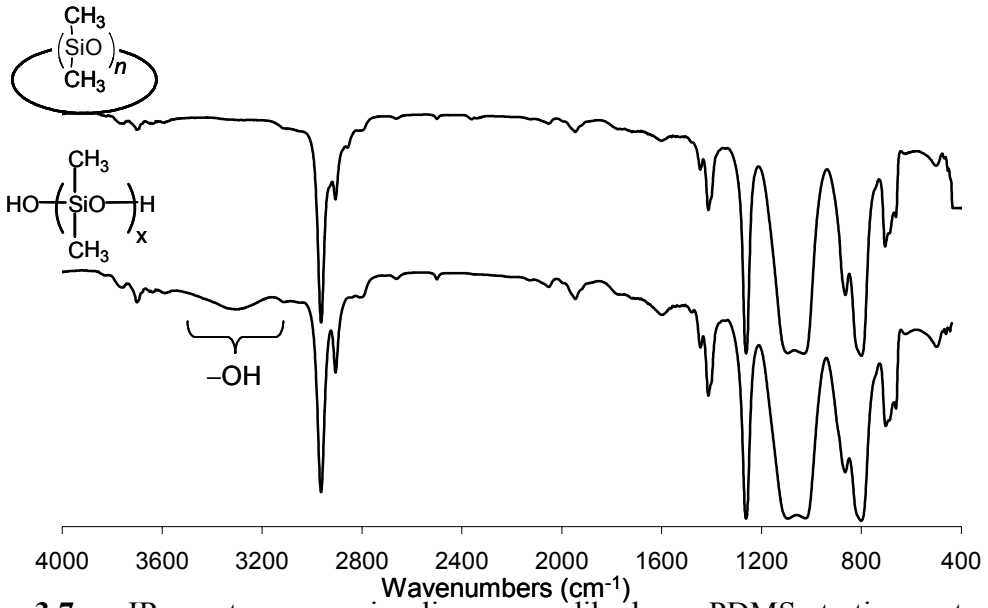


Figure 3.7 – IR spectra comparing linear α,ω-dihydroxy-PDMS starting material with the product of the cyclization scheme shown above, demonstrating the disappearance of the silanol end groups over the range 3120–3470 cm^{-1}.

Disappearance of the end groups was also apparent from ^{29}Si NMR. The spectrum of the starting material contained a major peak at -22.1 ppm due to internal silicons, and downfield peaks due to silicons adjacent to hydroxyl end groups (e.g., at -11.2 ppm).[23] These downfield peaks were completely absent in the product spectrum. The major peak in the product spectrum has been assigned to PDMS rings containing $n \geq 15$ repeat units, and the small upfield peaks have been attributed to smaller cycles ($n = 5–14$).[24]

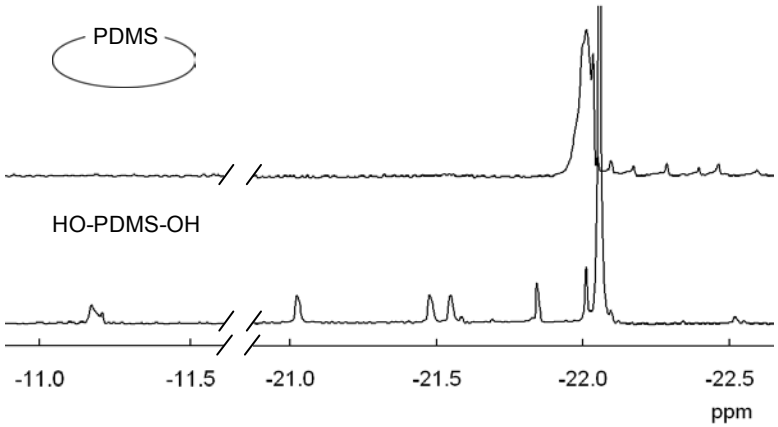


Figure 3.8 – ^{29}Si NMR spectra comparing linear α,ω-dihydroxy-PDMS starting material with the product of the cyclization scheme, demonstrating the disappearance of the silanol end groups.

While NMR and IR spectroscopy clearly indicated that the hydroxyl end groups disappeared, they did not provide independent evidence that cyclization had occurred. For this, GPC and MALDI-TOF mass spectrometry were used. GPC chromatograms and selected portions of MALDI-TOF spectra are shown in Figure 3.9 for the linear starting material (a), purified product (c), and also for a product prepared using the previously standard procedure of quenching the reaction with methanol (b). For both the resin-quenched (c) and methanol-quenched products (b), the data were collected after vacuum distillation of the product mixture. Vacuum distillation is used to remove the low-molecular-weight byproducts resulting from polymerization of the dichlorodimethylsilane coupling agent, and from back biting reactions of the end-group silanolates.

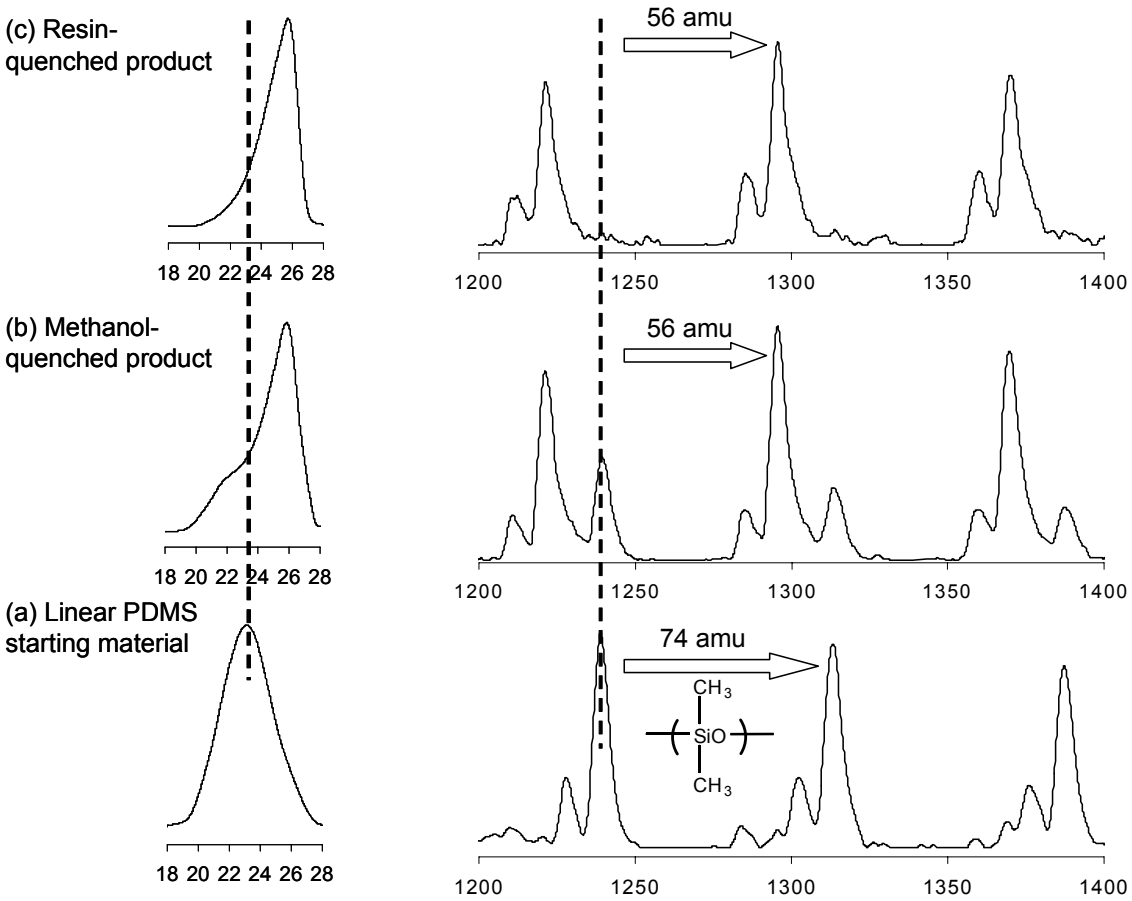


Figure 3.9 – GPC chromatograms and selected regions of MALDI-TOF mass spectra for (a) α,ω-dihydroxy-PDMS linear starting material, (b) methanol-quenched product, and (c) resin-quenched product of cyclization scheme. For both products, data shown were collected following vacuum distillation.

The GPC chromatograms are shown as signal intensity (differential refractive index) *versus* elution time. The hydrodynamic volumes of cyclic polymers are smaller than those of analogous linear polymers (i.e., same repeat-unit structure and molecular weight).[1] In GPC, decreased hydrodynamic volumes lead to increased retention times, which is exactly what is observed for the reaction product. Thus, the product has been cyclized. Note in Figure 3.9(b) that a short-retention-time shoulder on the chromatogram for the methanol-quenched product signifies the presence of linear byproducts. The

chromatogram for the resin-quenched product does not contain this broad shoulder thereby signifying a much cleaner cyclic product. Several attempts were made to remove the linear byproducts in the methanol-quenched product by repeated fractional precipitations using acetone-methanol solvent mixtures; these were unsuccessful. Attempts were also made to decrease the fraction of linear byproducts in the crude product mixture by (1) increasing the stoichiometric excess of NaH, (2) increasing the stoichiometric excess of the dichlorosilane coupling agent, or (3) decreasing the concentration of starting material to 10^{-4} M; these were also unsuccessful.

In fact, the MALDI-TOF spectral regions clearly show that all linear anionic species are efficiently removed by ion-exchange reactions with the macroporous anion-exchange resin.

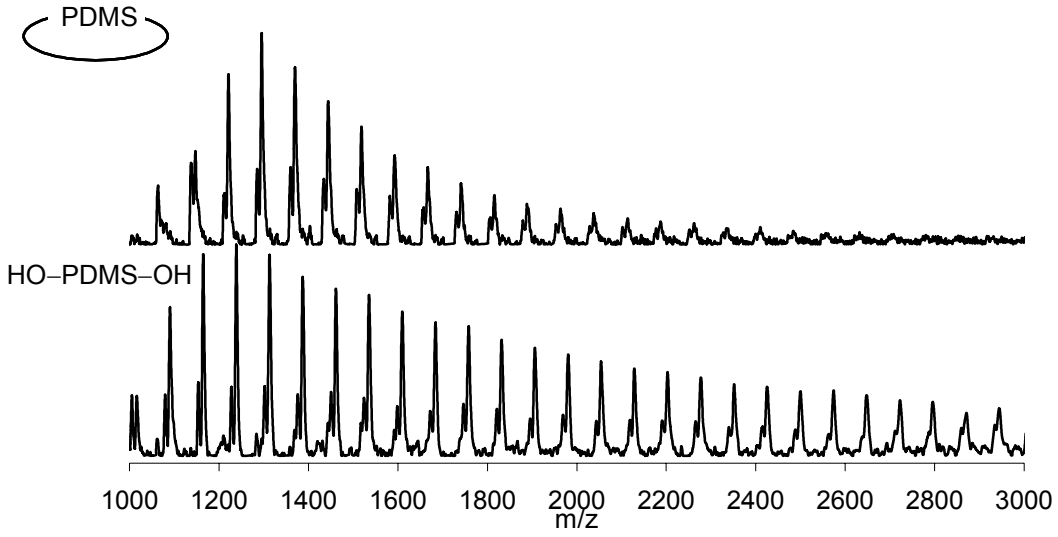


Figure 3.10 – MALDI-TOF spectra comparing linear α,ω-dihydroxy-PDMS starting material with the product of the cyclization scheme shown above demonstrating that a shift to higher molecular weights, which would have been indicative of chain-extension, was not observed.

The full MALDI-TOF spectra from which the regions of Figure 3.9 (a) and Figure 3.9 (c) are selected contain the characteristic envelope of peaks representative of polydisperse synthetic polymers. However, the molecular weight distribution of the starting material is slightly broader than that of the cyclic product, which does not contain some of the higher-molecular-weight species. From GPC, the polydispersity indices are 1.88 for the starting material and 1.35 for the cyclic product. Either the low-molecular-weight PDMS is cyclized more efficiently than the longer chains, or some siloxane bonds are cleaved by the end-group silanolates, or both. The asymmetric GPC chromatogram of Figure 3.9 (c) presumably results from these effects, perhaps coupled with some loss of lower-molecular-weight cycles during the vacuum distillation step.

The MALDI-TOF spectral region containing the most intense peak of the distribution is shown in Figure 3.9 (a) for the linear starting material. This peak appears at 1239 amu and corresponds to a silver-cationized α,ω-dihydroxy-PDMS species containing 15 dimethylsiloxy repeat units.[25] The minor peak just to the left of the most intense peak represents a sodium-cationized[26] α,ω-dihydroxy-PDMS species.[27] The three major peaks shown in Figure 3.9 (a) (and also the three minor peaks) are separated by 74 amu, which is the mass of a PDMS repeat unit.

Peaks due to linear starting material appear in the MALDI-TOF spectral region of Figure 3.9 (b) for the methanol-quenched product, but not in the spectrum for the resin-quenched product shown in Figure 3.9 (c). *Thus, resin quenching is an efficient means to remove linear byproducts*. The major product is clearly cyclic PDMS. The methanol-quenched product contains cyclic PDMS as well as linear byproducts, as indicated by the overlapping sets of peaks in its mass spectrum. The resin-quenched product contains

peaks due to the cyclic PDMS only, each separated from its subsequent homolog by 74 amu.

3.3.2 Cyclization beginning with α,ω-dihydroxy-PDMS (M_n~4,200 g/mol) and α,ω-dihydroxy-PDMS (M_n~6,000 g/mol) linear precursors

The cyclization scheme of α,ω-dihydroxy-PDMS as previously discussed was applied to longer linear precursors with the objective of synthesizing larger cycles. Therefore, α,ω-dihydroxy-PDMS of larger molecular weights, M_n~4,200 g/mol and M_n~6,000 g/mol, were subjected to identical cyclization methods as described for M_n~2,400 g/mol. Much to our surprise, the kinetically-controlled product was not produced; all of the cyclic products had identical GPC retention times indicating that a thermodynamic product had formed.

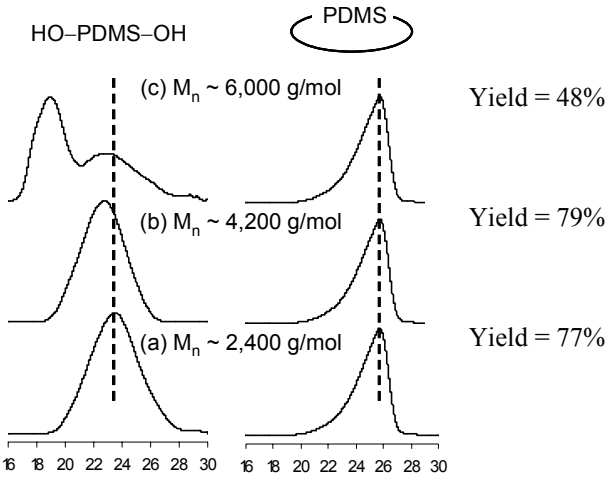


Figure 3.11 – GPC chromatograms for linear and cyclic PDMS from three different molecular weights of α,ω-dihydroxy-PDMS: (a) M_n~2,400 g/mol, (b) M_n~4,200 g/mol, and (c) M_n~6,000 g/mol. For all products, data shown were collected following vacuum distillation.

In the research conducted on the ring-chain equilibration process of cyclic PDMS, Brown and Slusarczuk described the stability of various sizes of PDMS rings under strongly basic condition. D_4 and D_5 were heated under neat conditions in the presence of KOH for several days to yield linear PDMS and a distribution of cyclic PDMS (see Figure 3.12). That distribution was characterized and a relationship between log K_n, where K_n is a molar cyclization constant, and the ring size of siloxane units, n, is shown in Figure 3.13. This plot of -log K_n *versus* n shows a stability maximum at D_4, a local minimum at D_{12}, and a local maximum at D_{15}.[3]

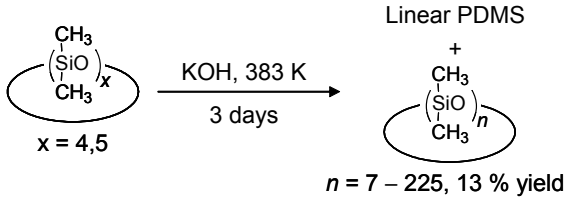


Figure 3.12 – Synthesis of cyclic PDMS in 13% yield by ring-chain equilibration beginning with cyclic siloxanes D_4 and D_5.[3]

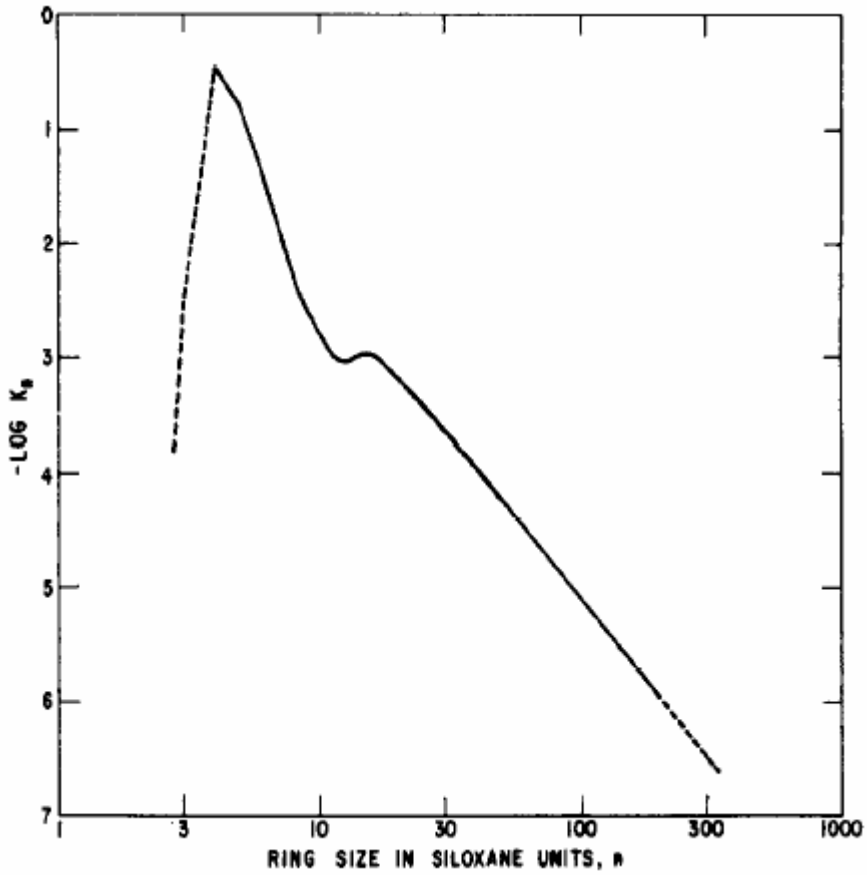


Figure 3.13 – The stability of PDMS cycles during ring-chain equilibration is described by the molar cyclization constant, K_n, which is dependent on the number of siloxane repeat units, n. Over the range 24–46 atoms (n = 12–23 repeat units) within the siloxane rings, a local maximum is reached at 30 atoms (n = 15 repeat units). [Reprinted with permission from Brown, J. F.; Slusarczuk, G. M. *J. Am. Chem. Soc.* **1965**, *87*, 931. Copyright 1965 American Chemical Society.]

The linear relationship observed for the largest rings (n > 15 repeat units) represents an experimental verification of the Jacobsen-Stockmayer cyclization theory,[28] which states that chain-ends from longer chains are less likely to interact with one another when compared to chain-ends of shorter chains with the same chemical structure. The deviations of the smaller-ring K_n values suggest that PDMS chains do not act as polymers in solution with a random distribution of end-to-end segment distances until the chain segments are longer than thirty atoms long. In fact, at n = 15 repeat units, the

PDMS chain is at such a length as to encourage end-to-end interactions relative to other lengths when $n > 10$.[3]

Cyclic PDMS prepared from α,ω-dihydroxy-PDMS in the presence of a base under dilute solution conditions was analyzed by MALDI-TOF and a relationship was also observed for -log K_n versus n, where K_n is the concentration of cyclic PDMS of a particular number of repeat units, n, relative to the total concentration of cycles.

$$K_n = \frac{[Cycle_n]}{[Cycle_{total}]} \qquad \{1\}$$

A preference was found for cycles of size $n = 16$ repeat units, but for $n > 16$, a region of steepening slope was not observed.

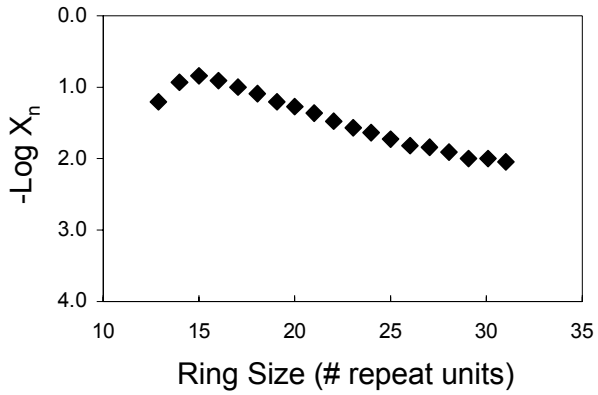


Figure 3.14 – The concentration of PDMS cycles formed after deprotonating α,ω-dihydroxy-PDMS in dilute solution conditions is described here by X_n. Over the range 24–64 atoms (n = 12–32 repeat units) within the siloxane rings, a maximum is reached at 32 atoms (n = 16 repeat units).

The mechanism for this observed behavior appeared to be due to backbiting by the anionically-charged end. Siloxanes have long been known for their backbiting behavior, but no studies had discussed the nature of this phenomenon, especially under these conditions. Most studies have observed siloxanes under neat conditions or in concentrated solutions, but under dilute conditions each chain is prohibited from interacting with other chains. No polymerization occurred through chain-extension, which verified that each PDMS chain did not interact with other chains. Therefore, the product formed is the product formed only through a chain's possible interactions with itself, a base, and a coupling agent.

The nature of the sodium hydride base as compared to KOH is particularly important. Oxygen and silicon atoms have a strong affinity for one another, so KOH as a base not only deprotonates the hydroxyl-terminated PDMS, but $^{-}$OH also reacts directly with PDMS chains to cause chain scission or with PDMS cycles to cause ring opening. Sodium hydride produces neither of the effects.

To provide evidence of cyclization either through backbiting or via a coupling agent, α,ω-dihydroxy-PDMS (M_n~2,400 g/mol) was deprotonated by sodium hydride in dilute solution and stirred at room temperature for 96 hours without adding dichlorodimethylsilane. The reaction was monitored by GPC, which demonstrated a shift to longer retention times even after just 26 hrs. This shift is indicative of cyclization. A shoulder is apparent in the sample removed after 26 hrs, but after 96 hrs in solution, this shoulder seems to have completely disappeared.

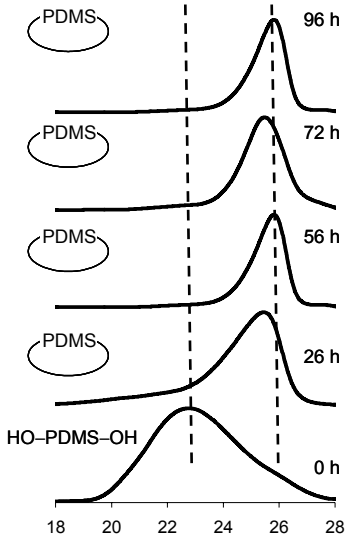


Figure 3.15 – GPC chromatograms of α,ω-dihydroxy-PDMS (M_n~2,400 g/mol), and the product of deprotonating the linear starting material with sodium hydride in dilute solution. GPC demonstrated a shift to longer retention times even after just 26 hrs, indicating cyclization without the need of a coupling agent. All data were collected after vacuum distillation.

3.4 CONCLUSIONS

Cyclic PDMS was cyclized and efficiently purified by the addition of a macroporous anion-exchange resin. Cyclization was monitored by IR and ^{29}Si NMR, which indicated the disappearance of the hydroxyl end-groups. This information did not provide conclusive evidence of cyclization, so the product was analyzed by GPC and MALDI-TOF. GPC demonstrated an increase in retention time for the product, which is indicative of cyclization, while MALDI-TOF exhibited peaks that corresponded to the mass of cyclic PDMS plus the mass of the ionizing agent. IR, ^{29}Si NMR, GPC, and MALDI-TOF conclusively proved the formation of cyclic PDMS.

GPC and MALDI-TOF were also capable of determining the purity of the cycles. A shoulder in the GPC chromatogram indicated the presence of uncyclized starting material within the product quenched by methanol, and MALDI-TOF displayed peaks representative of the linear precursor. This evidence confirmed the effectiveness of the macroporous anionic exchange resin as a means to remove charged species from a reaction.

α,ω-Dihydroxy-PDMS of higher molecular weights (M_n~4,200 and 6,000 g/mol) were subjected to identical conditions as described for α,ω-dihydroxy-PDMS (M_n~2,460 g/mol), but larger PDMS cycles were not synthesized. Cyclic PDMS (n = 16 repeat units) was formed preferentially giving credence to a hypothesis that backbiting of the linear PDMS chain was occurring and providing the cyclic product without using the coupling agent. Therefore, α,ω-dihydroxy-PDMS (M_n~2,460 g/mol) was deprotonated in dilute solution, but no coupling agent was added. GPC indicated that cyclic product resulted.

3.5 REFERENCES

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(25) 108 amu (Ag) + 18 amu (end groups) + n(74 amu (repeat unit) = 1239 amu; x = 15 repeat units.

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CHAPTER 4

CHARACTERIZATION OF PS-BLEND-CYCLOPDMS

4.1 INTRODUCTION

True polyrotaxanes require cyclic molecules to be threaded onto polymer segments that contain bulky end groups to block dethreading of the cyclic component, but polypseudorotaxanes, which lack these blocking groups, have been reported as well for polymers threaded by crown ethers. Poly(methyl acrylate) (PMA) and poly(methyl methacrylate) (PMMA) have been threaded by 30c10 to produce pseudorotaxanes. As shown in Figure 4.1 for PMMA-*pseudorotaxa*-30c10, rotaxanated polymers were synthesized by azobisisobutyronitrile (AIBN)-initiated free-radical bulk polymerizations of the monomers in the presence of 30c10. Once the polymers were formed, they were dissolved in THF and precipitated into water to remove any crown ethers which were not physically bound to the polymer backbones through rotaxanation. Threading up to 3.8 mass % and 1.7 mass % for PMA-*pseudorotaxa*-30c10 and PMMA-*pseudorotaxa*-30c10, respectively, were obtained.[1]

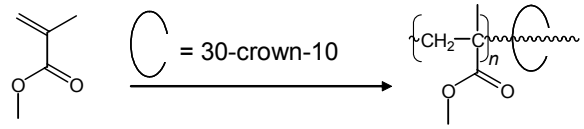
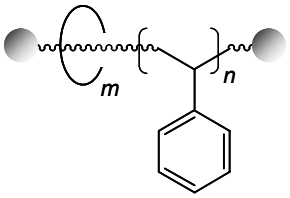


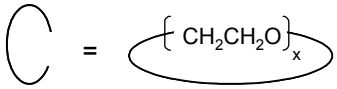
Figure 4.1 – Synthetic scheme for the synthesis of PMMA-*pseudorotaxa*-30c10, which yielded the crown ether being threaded in 1.7 mass %.

Under these conditions, no thermodynamic driving forces were present to promote threading. Rotaxanation occurred statistically where the macrocycles were simply added during the polymerization as additives and they became physically trapped onto the polymer backbone. As a result, low threading yields were observed, but even small amounts of an additive have been shown to have an effect on the physical properties of a polymer.

A true rotaxane, poly(styrene-*rotaxa*-crown ethers), was synthesized by initiating the polymerization of styrene with diazo-based blocking groups in the presence of crown ethers with toluene utilized as a cosolvent. The diazo-based blocking groups proved effective for preventing crown ethers as large as 42-crown-14 from dethreading. Once the rotaxane was formed, the polymer was dissolved in toluene and precipitated into methanol to remove any unthreaded crown ethers. As shown in Figure 4.2, the weight percent of crown ethers incorporated into the rotaxane was directly related to the sizes of the cycles.



Poly(styrene-*rotaxa*-crown ether)



Ring Size (# atoms)	Threaded?	Mass % Cycles
18	No	-
30	Yes	1.4 %
34	Yes	3.5 %
42	Yes	21.0 %

Figure 4.2 – A true rotaxane of poly(styrene-*rotaxa*-crown ethers) was prepared by initiating the polymerization with diazo-based free-radical initiators that left PS with end-caps to prevent crown ethers as large as 42c14 from dethreading. The weight percent of crown ethers incorporated into the rotaxane was directly related to the size of cycle.

With these results in mind, attempts were made to synthesize poly(styrene-*pseudorotaxa*-cycloPDMS) by polymerizing styrene via AIBN-initiation in the presence of cyclic PDMS (n = 16 repeat units, 32 atoms in circumference) as shown in Figure 4.3. Once the polymer was synthesized, it was dissolved in toluene and precipitated into a solvent for cyclic PDMS, *tert*-butanol/ethanol (*t*-BuOH/EtOH, 90:10), to remove unthreaded cyclic PDMS. Initial attempts proved unsuccessful, so adaptations were made to promote threading.

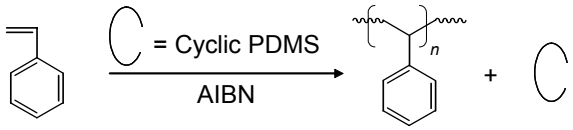


Figure 4.3 – Synthetic scheme for the synthesis of PS-*pseudorotaxa*-cycloPDMS.

Initially, styrene and cyclic PDMS were miscible and formed a single clear phase, but as polymerization proceeded, polymerization-induced phase segregation (PIPS) occurred. Therefore, toluene was added as a cosolvent to maintain homogeneity throughout polymerization. To alleviate concerns regarding dethreading of cyclic PDMS in solution, diazo-based blocking-group initiators were synthesized and used to polymerize styrene in the presence of cyclic PDMS. Polystyrene terminated predominantly (> 95%) through coupling, which left a polymer with both ends capped to prevent dethreading of any incorporated cyclic species. All of the polymerizations were heated to 90 °C to dissociate the diazo-compounds, so some of the reactions were performed in a closed system in order to increase the pressure on the solution. This was done to promote interactions of the linear and cyclic components. None of these modifications to the original experimental procedure were successful, so larger cyclic PDMS (n = 58 repeat units, 116 atoms in circumference) was subjected to these reactions conditions. These reactions did not produce a *pseudo*- nor a true rotaxane as the cyclic PDMS was always washed from the polymer mixture during the precipitation process.

Polymer blends of PS and cyclic PDMS were studied as films, which were cast by spin-coating toluene solutions of the blends onto microscope slides. The samples were annealed and the surface properties were evaluated by contact angle measurements.

4.2 EXPERIMENTAL PROCEDURE

4.2.1 Materials

All reagents were used as received unless otherwise noted. *p-tert*-Butylbromobenzene (98%), 4,4'-azobis(4-cyanopentanoic acid) (75%), hexane (HPLC grade, 95%), heptane (HPLC grade, 99%), thionyl chloride (99%), hydrochloric acid (ACS grade, 37%), magnesium turnings (98%), methanol (98%), methyl *tert*-butylbenzoate (99%), methylene chloride (anhydrous, 99.8%), phenol (99%), tetrahydrofuran (anhydrous, 99.9%), tetrahydrofuran (HPLC grade, 99%), and toluene (anhydrous, 99.8%) were purchased from Aldrich. Styrene (99%) was purchased from Aldrich and purified by subjecting the monomer to a *tert*-butylcatechol-removal column to remove the inhibitor, drying over CaH_2 and distilling by vacuum distillation. "Instant Ocean" was purchased from PetSmart. Cyclic PDMS (n = 16 repeat units) was prepared as previously discussed. Cyclic PDMS (n = 58 repeat units) was used as received from Stephen Clarson at the University of Cincinnati.

4.2.2 Instrumentation

IR spectroscopy was performed on a Bruker Vector 22. Liquid samples were analyzed on KBr salt plates and solid samples were analyzed by making pellets with KBr. GPC was conducted in THF (1 ml/min) at 303 K on three Waters Styragel columns (5 μm beads: HR 1, 100 Å, HR 3, 1000 Å, HR 4, 10,000 Å) that were connected to a Waters 2690 separations module and Waters 2410 refractive index detector. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AMX 400 in $CDCl_3$ at room temperature. ^{1}H NMR were conducted on a Bruker DRX-500 in $CDCl_3$ at room temperature. Contact angle

measurements required polymer films, which were solution-cast from toluene, and analyzed on a VCA 2500XE video contact angle system from AST Products, Inc. Advancing angle measurements were obtained through successive drops of 1 μL.

4.2.3 Synthesis

Glassware was dried at 120 °C overnight; all liquid transfers occurred via gastight syringes unless otherwise noted.

Tris(p-tert-butylphenyl)methanol.

Into an oven-dried 1-L, three-neck flask equipped with stir bar, condenser, and nitrogen inlet were placed magnesium turnings (9.60 g, 0.40 mol) in THF (650 ml). *p-tert*-Butylbromobenzene (44.0 ml, 0.26 mol) in THF (100 ml) was added dropwise via syringe pump over the course of 1 hr with gentle heating. The reaction was stirred for 2 hrs until a brown color was observed. Methyl *tert*-butylbenzoate (23.0 ml, 0.12 mol) in THF (100 ml) was added dropwise via syringe pump over the course of 1 hr. After refluxing overnight, the solution was cooled to room temperature and neutralized with 10% HCl until the mixture became a transparent solution. Product was extracted with heptane (3×150 ml), and the combined organic phases were washed with water (3×300 ml), then dried over magnesium sulfate. A yellow solid was obtained after removing the solvent by rotary evaporation. The product was purified by recrystallizing twice from methanol to yield a white powder (37.86 g, 74 %). ^{1}H NMR: 1.30 (s, 27H, CH_3), 2.71 (s, 1H, OH), 7.18 (dd, 6H, arom), 7.31 (dd, 6H, arom). ^{13}C NMR: 31.40, 34.47, 81.55, 124.72, 127.59, 144.26, 149.84.

Tris(p-tert-butylphenyl)(4-hydroxyphenyl)methane.

Into an oven-dried 250-ml, three-neck flask equipped with a stir bar, condenser, and nitrogen inlet was added *tris*(*p-tert*-butylphenyl)methanol (24.67 g, 0.057 mol). Phenol (104.0 g, 1.11 mol) was added and the alcohol was dissolved by warming the mixture. Once solution was established, concentrated HCl (2.0 ml, 0.0229 mol) was added as a catalyst. A deep reddish-blue color was observed immediately. After refluxing overnight, the solution was cooled to room temperature. Product was extracted with toluene (3×150 ml), and the combined organic phases were washed with aqueous NaOH solution (3×250 ml), washed with water (3×350 ml), and dried over magnesium sulfate. A white powder (19.40 g, 0.038 moles, 67%) was obtained after recrystallizing twice from a toluene/hexane solution (3:2). ^{1}H NMR: 1.30 (s, 27H, CH_3), 6.72 (d, 2H, arom), 7.02 (d, 2H, arom), 7.08, 7.22 (2d, 12H, arom).

meso-4,4'-Azobis[4-cyanopentanoyl chloride].

Recrystallization from ethyl alcohol and ethyl acetate separated 4,4'-azobis[4-cyanopentanoic acid] into two isomeric forms, one melting at 141-143 °C and the other at 125-127 °C. The lower melting isomer was used to form the blocking-group initiator.

Into a 50-mL, 2-necked flask equipped with a stir bar, condenser, and nitrogen inlet was added meso-4,4'-azobis[4-cyanopentanoic acid] (2.00 g, 7.14 mmol) and thionyl chloride (40 mL, 550 mmol). The mixture was placed in a preheated oil bath at 100 °C. After 10 min, the mixture was placed in an ice bath. The solution was cooled to room temperature, and the excess thionyl chloride was removed by vacuum. The resulting solid was dissolved in warm benzene and precipitated with pentane. The solid

was filtered under a nitrogen blanket and dried in a vacuum desiccator to yield 2.0 g (88%) of a white powder. ^{1}H NMR ($CDCl_3$, ppm): 1.55 (s, 6H), 2.45 (m, 4H), 3.05 (m, 4H). ^{13}C NMR ($CDCl_3$, ppm): 23.57, 32.91, 41.77, 71.24, 116.90, 172.15.

meso-p-[Tris(p-tert-butylphenyl)methyl]phenyl 4,4'-azobis[4-cyanopentanoate] (daBG).

Into a 100-mL, 3-necked flask equipped with a stir bar and nitrogen inlet were dissolved *tris*(*p-tert*-butylphenyl)-(4-hydroxyphenyl)methane (1.744 g, 3.5 mmol) and pyridine (0.35 ml, 4.3 mmol) in THF (20.0 ml). *meso*-4,4'-Azobis(4-cyanopentanoic acid chloride) (0.491 g, 1.50 mmol) in benzene (25.0 mL) was added dropwise over 10 min. via syringe pump. During this time the reaction mixture became cloudy, and a white precipitate formed. After 4 h the mixture was filtered, and hexane was added. The organic layer was washed with water (3 × 25 mL) and dried over magnesium sulfate. The organic solvents were removed, and the sample was dried under vacuum to yield 1.70 g (88%) of a white powder. ^{1}H NMR ($CDCl_3$, ppm): 1.28 (s, 36H), 1.43 (m, 4H), 1.55 (s, 6H), 2.25-2.65 (m, 12H), 4.01 (t, J = 5.8 Hz, 4H), 7.15 (m, 26H). ^{13}C NMR ($CDCl_3$, ppm): 23.6, 25.3, 29.2, 31.3, 33.2, 34.4, 36.6, 55.4, 65.6, 71.7, 117.6, 124.6, 127.7, 128.7, 129.0, 144.0, 147.0, 148.0, 171.0.

General polymerization procedure under ambient pressure (PS 1).

Into an oven-dried test tube equipped with a stir bar and rubber septum was added AIBN (0.0081 g, 0.05 mmol) under constant flow of argon. The tube was purged by vacuum and argon backfill (×2), followed by the addition of styrene (0.50 ml, 4.3 mmol) and cyclic PDMS (n = 16, 3.5103 g) via syringe. The mixture was purified of dissolved

gases by repeated freeze-pump-thaw degassing (×3) in liquid nitrogen until no bubbles were seen after thawing. The tube was warmed to room temperature, backfilled with N_2 gas, then placed in a preheated oil bath at T = 90 °C. The mixture was stirred under argon until the polymer solidified and stirring was unable to continue (24–48 hrs). The sample was dissolved in toluene (5 ml) then precipitated into a solution of *t*-BuOH/EtOH (90:10, 100 ml). The solid polymer was filtered and dried under vacuum, then analyzed by ^{1}H NMR. This was repeated several times (3–7) until PDMS was no longer evident in the ^{1}H NMR spectrum.

PS 3.

AIBN (0.0190 g, 0.12 mmol), styrene (0.50 ml), toluene (2.0 ml) and cyclic PDMS (n = 16, 2.0 mmol).

PS 5.

daBG (0.0409 g, 0.033 mmol), styrene (0.50 ml, 4.3 mmol), and cyclic PDMS (n = 16, 0.5 ml, 0.39 mmol).

PS 7.

daBG (0.0478 g, 0.038 mmol), styrene (0.50 ml, 4.34 mmol), toluene (1.0 ml) and cyclic PDMS (n = 16, 0.5 ml, 4.34 mmol)

PS 9.

AIBN (0.0018 g, 0.011 mmol), styrene (0.50 ml, 4.34 mmol), and cyclic PDMS (0.10 ml, 0.023 mmol).

PS 11.

AIBN (0.0015 g, 0.0091 mmol), styrene (0.50 ml, 4.34 mmol), toluene (1 ml), and cyclic PDMS (0.10 ml, 0.023 mmol)

PS 13.

daBG (0.0092, 0.0073 mmol), styrene (0.50 ml, 4.34 mmol), and cyclic PDMS (0.10 ml, 0.023 mmol).

PS 15.

daBG (0.0109 g, 0.0087 mmol), styrene (0.50 ml, 4.34 mmol), toluene (1.0 ml), and cyclic PDMS (0.10 ml, 0.023 mmol).

General polymerization procedure under increased pressure (PS 2).

Into a double-walled test tube, which was able to withstand pressures up to 60 psig and equipped with a stir bar and rubber septum, AIBN (0.0021 g, 0.013 mmol) was added followed by the addition of styrene (0.50 ml, 4.34 mmol) and cyclic PDMS (1.0 ml, 0.75 mmol) via syringe. The mixture was purified of dissolved gases by repeated freeze-pump-thaw in liquid nitrogen until no bubbles were evident after the thaw. The tube was backfilled with an inert gas, warmed to room temperature, capped with a Teflon

screwcap, and then placed in a preheated oil bath at 90 °C. The mixture was stirred until the polymer solidified and stirring was unable to continue (24–48 hrs). The product was dissolved in toluene (20 ml), and precipitated into a solution of *t*-BuOH/EtOH (90:10, 200 ml) to remove any unthreaded cyclic PDMS. The polymer was filtered and dissolved in toluene (10 ml) followed by precipitation into a solution of *t*-BuOH/EtOH (90:10, 100 ml). This was repeated (3–7 times) until no cyclic PDMS remained in the polymer according to ^{1}H NMR.

PS 4.

AIBN (0.0016 g, 0.0097 mmol), styrene (0.50 ml, 4.34 mmol), toluene (1.0 ml), and cyclic PDMS (1.0 ml, 0.75 mmol)

PS 6.

daBG (0.0097 g, 0.0077 mmol), styrene (0.50 ml, 4.34 mmol), and cyclic PDMS (1.0 ml, 0.75 mmol).

PS 8.

daBG (0.0101 g, 0.0081 mmol), styrene (0.50 ml, 4.34 mmol), toluene (1.0 ml), and cyclic PDMS (1.0 ml, 0.75 mmol).

PS 10.

AIBN (0.0025 g, 0.015 mmol) styrene (0.50 ml, 4.34 mmol), and cyclic PDMS (0.10 ml, 0.023 mmol).

PS 12.

AIBN (0.0011 g, 0.0067 mmol), styrene (0.50 ml, 4.34 mmol), toluene (1.0 ml), and cyclic PDMS (0.10 ml, 0.023 mmol).

PS 14.

daBG (0.0075 g, 0.0060 mmol), styrene (0.50 ml, 4.34 mmol), and cyclic PDMS (0.10 ml, 0.023 mmol).

PS 16.

daBG (0.0098 g, 0.0078 mmol), styrene (0.50 ml, 4.34 mmol), toluene (1 ml) and cyclic PDMS (0.10 ml, 0.023 mmol).

Preparation of PS-blend-cycloPDMS.

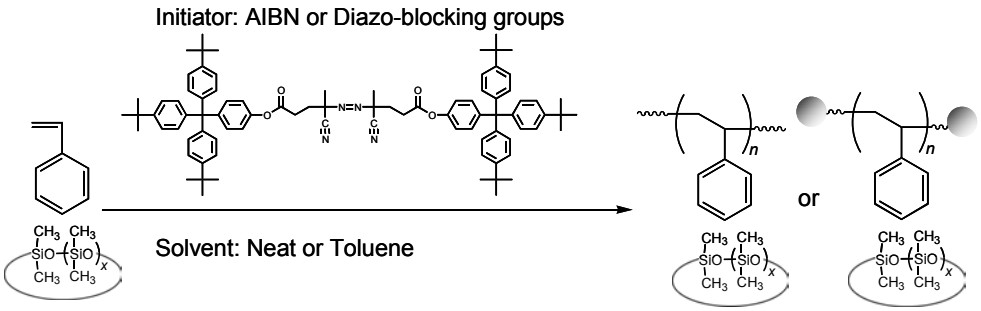
PS-*blend*-cycloPDMS was prepared by dissolving polystyrene (~0.5 g, M_n~74,000 g/mol, M_w~270,000 g/mol) and cyclic PDMS (n = 16 repeat units) in toluene (5 ml). Two blends were studied, including samples containing 0, 5, and 20% by weight of cyclic PDMS. Films were formed by spin-casting onto microscope slides, which had been cleaned with soap and water. Approximately 2 ml of solution was used to prepare each film. Solvent was removed by allowing the samples to dry under the hood for several minutes, and then the sample was annealed at 95 °C. Contact angle measurements were taken before the films were suspended in a stirring aqueous solution of "Instant Ocean" at room temperature. "Instant Ocean" is a salt mixture that provides

an aqueous environment similar to the ocean. The samples were removed from the bath and dried by lightly blowing inert gas across the film. Contact angle measurements were taken, and the films were annealed at 95 °C. This process of suspending the films in a stirring aqueous solution of "Instant Ocean", evaluating surface properties via goniometry, annealing the films, and evaluating the surface properties by goniometry again, was repeated twice.

4.3 RESULTS AND DISCUSSION

4.3.1 Initial work toward PS-pseudorotaxa-cycloPDMS (n = 16 repeat units).

Initial attempts toward incorporating cyclic PDMS onto a PS backbone were undertaken by subjecting cyclic PDMS to similar reaction conditions described for the synthesis of PS-*rotaxa*-crown ethers. Styrene was polymerized by AIBN in the presence of cyclic PDMS (n = 16 repeat units) under an inert atmosphere. After the reaction was stirred for ~24–48 hours at 90 °C, the polymer was precipitated into a solution of *t*-BuOH/EtOH (90:10), which was a good solvent for cyclic PDMS, to remove any unthreaded cyclic material. ^{1}H NMR was used to analyze the polymer sample and determine the cyclic PDMS content. The polymer was re-dissolved into toluene and precipitated a second time into a solution of *t*-BuOH/EtOH (90:10). ^{1}H NMR was again used to determine the cyclic PDMS content within the sample, and this process was repeated (~3−7 times) until the amount of cyclic PDMS within the polymer remained constant. In all cases, cyclic PDMS was removed during this clean-up process.



PS	Cycle size (# atoms)	Initiator	Solvent	Pressure
1	30	AIBN	Neat	No
2	30	AIBN	Neat	Yes
3	30	AIBN	Toluene	No
4	30	AIBN	Toluene	Yes
5	30	daBG	Neat	No
6	30	daBG	Neat	Yes
7	30	daBG	Toluene	No
8	30	daBG	Toluene	Yes

PS	Cycle size (# atoms)	Initiator	Solvent	Pressure
9	117	AIBN	Neat	No
10	117	AIBN	Neat	Yes
11	117	AIBN	Toluene	No
12	117	AIBN	Toluene	Yes
13	117	daBG	Neat	No
14	117	daBG	Neat	Yes
15	117	daBG	Toluene	No
16	117	daBG	Toluene	Yes

Figure 4.4 – Initial attempts toward PS-rotaxa-cycloPDMS, but after dissolving the final product in toluene and precipitating the polymer into t-BuOH/EtOH (90:10) several times to dissolve unthreaded cyclic PDMS, no PDMS remained in the product.

None of these initial attempts proved successful, so polymerization conditions were altered as described in Figure 4.4. Styrene and cyclic PDMS were miscible, but as polymerization occurred, the solution became opaque. Therefore, toluene was employed as a solvent to prevent PIPS. Another concern was that cyclic PDMS threaded onto the PS chains, but dethreaded during the precipitation process, so a diazo-based blocking group (daBG) was synthesized and utilized to produce end-capped PS by free-radical polymerization.

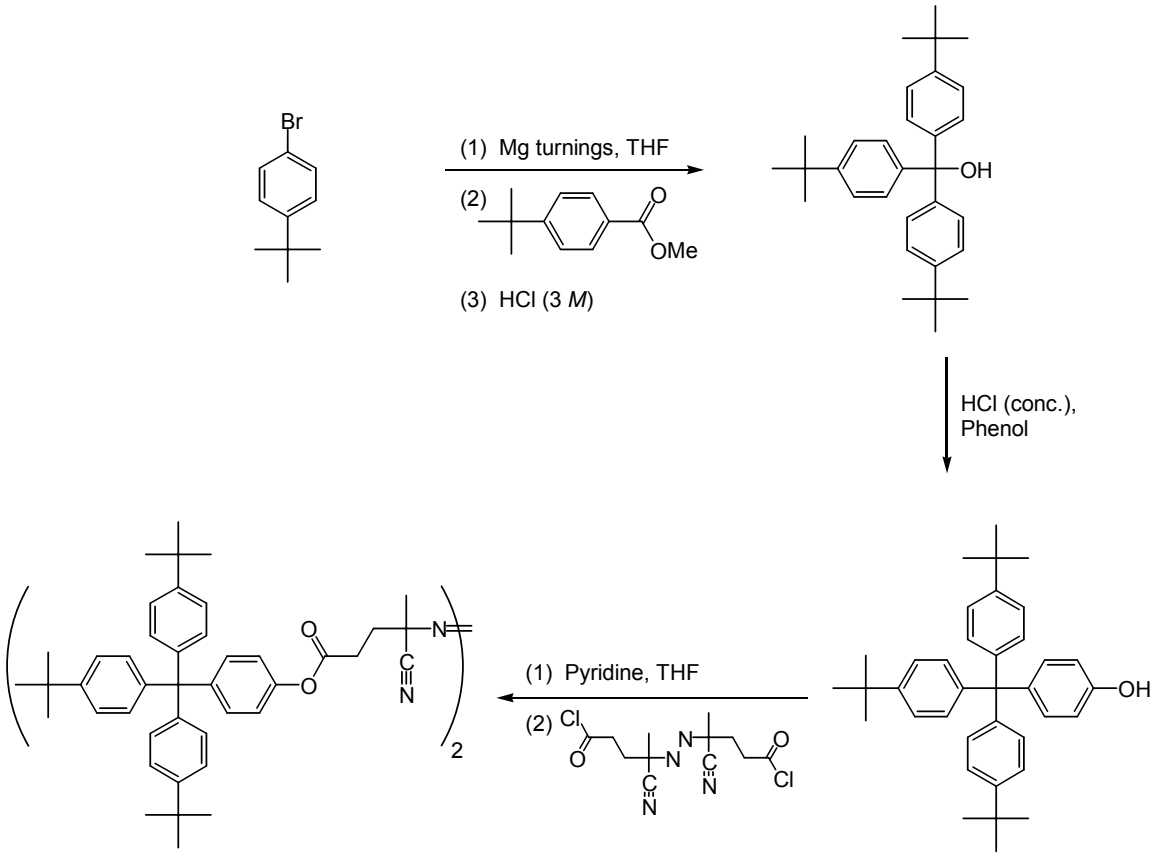


Figure 4.5 – Synthetic scheme detailing the synthesis of a diazo-based blocking group, *meso-p*-[*tris*(*p-tert*-butylphenyl)methyl]phenyl-4,4'-azobis[4-cyanopentanoate] (daBG), which was synthesized in 25% yield.

The synthesis of daBG included a Grignard addition of methyl *tert*-butylbenzoate to *p-tert*-butyl magnesium bromide. The resulting triarylmethanol can not be used directly as a blocking group because of the steric hindrance provided by the phenyl rings, and further chemistry forming trityl ether compounds yields products that are hydrolytically unstable due to the stable tertiary carbocation, which can be formed in aqueous environments. Therefore, this triarylmethanol was subjected to an electrophilic aromatic attack by phenol under strongly acidic conditions. Synthesis of daBG was completed in 25% total yield by reacting *tris(p-tert*-butylphenyl)(4-

hydroxyphenyl)methane with *meso*-4,4'-azobis[4-cyanopentanoyl chloride] in the presence of pyridine.

Styrene was polymerized by daBG under identical conditions as compared to styrene, which was polymerized by AIBN, but no evidence was found that cyclic PDMS was trapped onto PS. Polymerizations were also performed in double-walled test tubes sealed with Teflon screwcaps, which sealed the heated systems and induced an increase in pressure formed by heating the samples to 90 °C. The objective of this technique was to apply pressure and increase the mixing between styrene, PS, and cyclic PDMS, but this too yielded no threaded material. Though crown ethers as small in circumference as 30 atoms have been threaded, cyclic PDMS containing 32 atoms within the cycle was not threaded. This may have occurred because the PDMS collapsed upon itself and existed in solution as a globule unable to be penetrated by solvent, monomer, or polymer.

4.3.2 Initial work toward PS-pseudorotaxa-cycloPDMS (n = 58 repeat units).

Cyclic PDMS of various sizes has been trapped onto PDMS network structures by crosslinking hydroxyl-terminated PDMS with tetraethylorthosilicate in the presence of the cyclic diluents.[2-4] Small cycles, $n < 38$ repeat units, were not trapped because the linear chains were not able to thread through the small rings. However, cyclic polymers in the range $38 < n < 517$ were threaded with an increasing amount of the cyclic species topologically trapped into the networks as the ring size increased as depicted in Figure 4.6. The experimental results, which were explained by Monte Carlo simulations based on a standard rotational isomeric state model for the cyclic molecules, demonstrated that

the chance of a cycle trapped into the network depended strongly on the size of the cycle.[2,5-7] An advantage of this system is that linear PDMS chains interact with all of the PDMS chain segments (linear or cyclic) in the exact same manner, so no problems associated with microphase separation are endured.

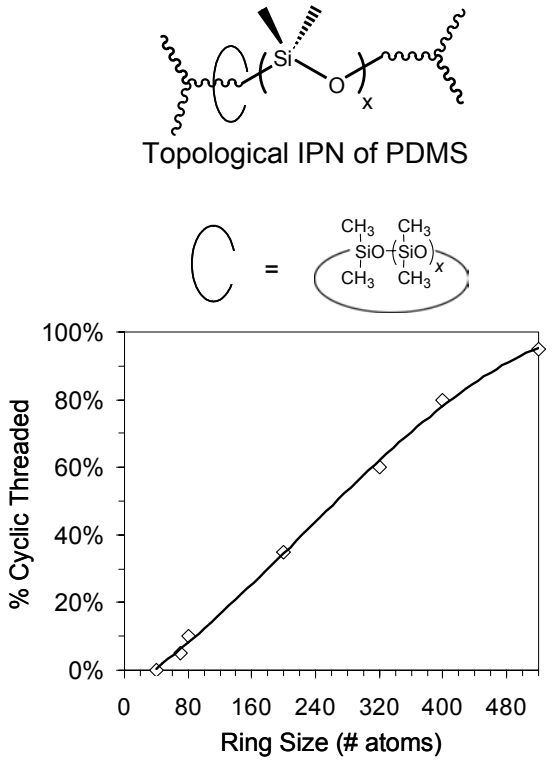


Figure 4.6 – The weight percentage of cyclic PDMS trapped within a PDMS network increases as the number of atoms within the ring increases.

Another example of cyclic PDMS being threaded by a polymer was demonstrated when poly(2,6-dimethyl-1,4-phenylene oxide) was crosslinked in the presence of cyclic PDMS (n = 32, 56, 92, and 110 repeat units) to physically trap 7, 20, 26, and 36% of the cycles, respectively, into the network. Phase separation was overcome by dissolving the

polymer in a 15-20% by weight solution of chloroform/toluene (10:90). After network formation, free cycles were removed via Soxhlet extraction in chloroform[8,9] Interestingly, cyclic PDMS (n = 31 repeat units) was not trapped onto a crosslinked network of PDMS, cyclic PDMS (n = 38 repeat units) was threaded onto a PDMS network in only 1% by weight, but cyclic PDMS (n = 32 repeat units) was reported as threaded onto crosslinked poly(2,6-dimethyl-1,4-phenylene oxide) in 7% by weight.

This led to our attempts of threading PS with a larger size of cyclic PDMS (n = 58 repeat units). The cyclic material was subjected to an identical set of reaction conditions as previously described for cyclic PDMS (n = 16 repeat units), but precipitating the polymer into a *t*-BuOH/EtOH solution always removed the cycles. These results were surprising when compared to literature, which described trapping PDMS cycles as small in circumference as n = 32 repeat units into crosslinked networks. The topological difference between a network and a polyrotaxane is that the blocking groups within a network can be viewed as infinitely large; once a cycle is threaded onto a chain that has been crosslinked, the cycle is permanently bound to that chain. A polyrotaxane, on the other hand, possesses blocking groups of finite size. Therefore, dethreading of cyclic PDMS over the bulky blocking groups may have occurred in solution.

4.3.3 Surface characterization of PS-blend-cycloPDMS.

Surface analysis of PS blends containing cyclic PDMS revealed invaluable information regarding the amount of PDMS necessary to change the surface properties of PS and the drawbacks of blend systems in general. Films of pure PS and PS-*blend*-cycloPDMS, which were solution-cast from toluene onto microscope slides, were

annealed and analyzed by goniometry. Advancing contact angles were measured by the successive additions of water (1 μL) onto the films.

A film of PS was analyzed after annealing and demonstrated an average contact angle of 94.5 ± 2.4°. As shown in Figure 4.7, blends of PS–cycloPDMS containing 5 and 20% PDMS by weight yielded contact angles of 103.8 ± 1.8° and 103.4 ± 1.1°, respectively, after the films were annealed at 95 °C overnight to allow cycloPDMS to segregate to the surface. The higher contact angle meant a surface more hydrophobic than PS was present. The samples were suspended in a stirred, aqueous solution of "Instant Ocean" overnight to determine the stability of the polymer surface. "Instant Ocean" was used as received from PetSmart to provide an aqueous environment similar to the ocean. The next morning, the films were removed from solution, dried by lightly blowing an inert gas over the films' surfaces, and annealed again at 95 °C. The average contact angle for the PS–cycloPDMS containing 20% PDMS by weight did not change within experimental error, but the average contact angle for PS–cycloPDMS containing 5% PDMS by weight decreased substantially to 95.9 ± 0.7°. The samples were subjected to the "Instant Ocean" solution and annealed a second time, and the average contact angle of the PS–cycloPDMS blend containing 5% by weight PDMS decreased further, while the average contact angle for the blend containing 20% cycloPDMS by weight showed no change. This blend was subjected to the "Instant Ocean" solution and annealed a third time, and finally the average contact angle decreased to 95.1 ± 1.5°, which was within experimental error of the average contact angle for a purely PS surface.

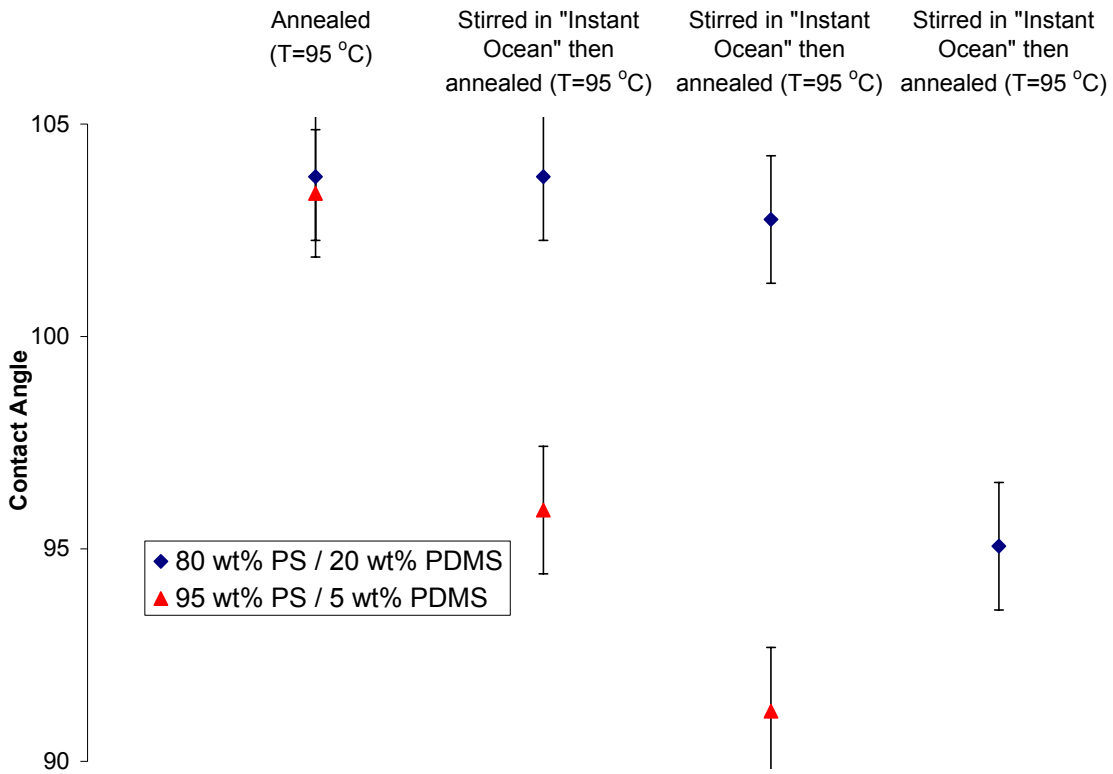


Figure 4.7 – Advancing contact angle measurements of PS-blend-cycloPDMS demonstrating that even 2 weight % of cyclic PDMS incorporated into PS has an effect on the surface properties of the film.

These results demonstrated the instability of polymer surfaces when the molecules at the surface are not physically or chemical bound to the base polymer. The sample containing the least amount of cyclic PDMS saw a fall in contact angle after being subjected to the "Instant Ocean" solution just a single time. This indicated that cyclic PDMS had been washed from the film surface and the surface was predominantly PS. The blends containing a higher content of cyclic PDMS also saw a decline in contact angle, but the fall was less dramatic. Apparently, cyclic PDMS moved to the surface when the film was annealed, but was washed away when the film was suspended in the solution of "Instant Ocean". In the sample containing a higher weight % of siloxanes, cyclic PDMS resided within the bulk as well as at the surface. Once the initial surface

was washed away, the siloxanes within the bulk segregated to the surface during annealing. This process continued until all of the cyclic PDMS was rinsed from the surface and no more siloxanated material was present in the bulk. Since the cycles were present as a blend, no physical entanglements deterred leaching.

4.4 CONCLUSIONS

Initial attempts toward incorporating cyclic PDMS onto a PS backbone were undertaken by polymerizing styrene in the presence of cyclic PDMS (n = 16 and 58 repeat units). Styrene was polymerized by AIBN and daBG, which was synthesized in 25% yield, in the presence of cyclic PDMS. Reaction conditions were altered by adding toluene as a cosolvent to prevent PIPS or by performing the reaction under pressure higher than ambient pressure. Once the polymer was formed, it was precipitated into a solution of *t*-BuOH/EtOH (90:10) to remove any unthreaded cyclic material. This process was repeated until all of the cyclic PDMS within the polymer system was removed, which indicated that PS-*rotaxa*-cycloPDMS was not present in solution.

Contact angle measurements of PS-*blend*-cycloPDMS demonstrated that even small amounts of cyclic PDMS (as low as 5% by weight) produced a more hydrophobic surface that pure PS. This result was important because low threading yields of cyclic PDMS onto PS were expected. Analysis of the blends also demonstrated the instability of the polymer surface; cyclic PDMS appeared to be leaching from the system because it was not physically nor chemically bound to the PS. The sample containing the least amount of PDMS saw a fall in contact angle after being suspended in the "Instant Ocean" solution just a single time. This indicated that cyclic PDMS had been washed from the

film surface and the surface was predominantly PS. The PS–cycloPDMS blend containing 20% by weight cyclic PDMS, also saw a decline in contact angle, but the fall was less dramatic because cyclic PDMS, which was previously present in the bulk, moved to the surface during annealing.

4.5 REFERENCES

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CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

5.1 CONCLUSIONS

- Perfluoro crown ethers, [F]-18c6 and [F]-30c10, were synthesized in ~80% and ~70% yield, respectively. ^{13}C NMR demonstrated a triplet of triplets for both [F]-18c6 and [F]-30c10, which were centered at 118.6 and 113.3 ppm, respectively, relative to TMS with *J*-coupling values of $^{1}J_{C-F}$ = 285 Hz and $^{2}J_{C-CF}$ = 45 Hz. The splitting pattern was due to coupling between the fluorines attached to the carbon atoms and splitting from the fluorines on the adjacent carbons.

- Cyclic PDMS (n = 16 repeat units) was synthesized in 80% yield from α,ω-dihydroxy-PDMS (M_n~2,460 g/mol) in the presence of sodium hydride and a coupling agent, dichlorodimethylsilane, under dilute solution conditions. IR and ^{29}Si NMR indicated the disappearance of the hydroxyl end-groups. GPC demonstrated a decreased retention time, which indicated cyclization, and MALDI-TOF exhibited peaks that corresponded to the mass of cyclic PDMS plus the mass of the ionizing agent.

- Cyclic PDMS was purified by a macroporous anion-exchange resin, which removed the charged, linear PDMS from solution. Cyclic PDMS was not lost during this purification step. Purity was determined by GPC and MALDI-TOF.

- α,ω-Dihydroxy-PDMS of higher molecular weights (M_n~4,200 and 6,000 g/mol) were cyclized in the presence of sodium hydride and dichlorodimethylsilane in dilute solution, but yielded cyclic PDMS (n = 16 repeat units).

- α,ω-Dihydroxy-PDMS (M_n~2,460 g/mol) was deprotonated in dilute solution, but dichlorodimethylsilane was not added to couple the chain ends. Cyclic PDMS (n = 16 repeat units) was produced.

- Attempts toward the synthesis of PS-*rotaxa*-cycloPDMS by polymerizing styrene with diazo-based initiators in a solution of cyclic PDMS (n = 16 repeat units) were unsuccessful even in toluene, a good solvent for the siloxane cycles. Cyclic PDMS seemed to be collapsed upon itself in such a manner that monomer did not swell the cycle, so the cavity was not penetrated by a polymer chain.

- Initial work of polymerizing styrene in the presence of cyclic PDMS (n = 58 repeat units) has not yielded PS-*rotaxa*-cycloPDMS. This may be because the blocking groups attached to the PS chains ends are not large enough to prevent dethreading of the cyclic siloxanes in solution.

- Contact angle measurements of PS-*blend*-cycloPDMS demonstrated a change to a more hydrophobic surface when as little as 5% by weight of the cycles were added.

- Blends of PS incorporating cyclic PDMS were demonstrated as having unstable surfaces. When the samples were suspended in an aqueous solution of "Instant Ocean" and then annealed, a decline in the contact angle was observed. This indicated that the surface was demonstrating more PS-like behavior due to cyclic PDMS leaching from the system.

5.2 RECOMMENDATIONS FOR FUTURE WORK

- Various crown ethers, including 30c10, have been threaded by polyesters to form rotaxanes. This threading process is driven by hydrogen-bonding between the oxygen atoms and hydroxyl-protons of the ethers and diols, respectively. [F]-30c10 does not possess this same affinity for hydroxyl-protons, but it is attracted to electronegative species. Experiments could be undertaken to equilibrate [F]-30c10 with deprotonated diols before adding the diacid chloride to form the polymer.

- The most intriguing development from this research was α,ω-dihydroxy-PDMS preferentially forming cycles of n = 16 repeat units. GPC demonstrated a shift in retention time from linear to cyclic PDMS after just 26 h. Further work should entail examining all of the species in solution using MALDI-TOF. Aliquots could be removed every hour from a dilute solution of deprotonated α,ω-dihydroxy-PDMS, quenched by methanol, and analyzed by MALDI-TOF to understand the change from linear precursor to cyclic product.

- Further work towards understanding this mechanism should involve subjecting other commercially-available α,ω-dihydroxy-siloxanes, such as poly(trifluoropropylmethylsiloxane) or poly(diphenylsiloxane), to determine the effect of substituents on this cyclization process.

- Surprisingly, cyclic PDMS as large in circumference as n = 58 repeat units did not form a rotaxane in solution. Literature has been published that states cycles of this size have been trapped onto polymer networks of PDMS and poly(phenylene oxide), so the cycles may have threaded onto PS chains and then dethreaded during the work-up. In this case, larger blocking groups, e.g., dendrimers, should be prepared as diazo-initiators to polymerize styrene and prevent dethreading of cyclic PDMS in solution.

- Proof that the styrene monomer penetrates cyclic PDMS (n = 58 repeat units) could be ascertained by adding divinylbenzene to the polymerization of styrene in the presence of cyclic PDMS. Any cycles threaded by PS would be unable to dethread because the network linkages would act as permanent blocking groups.

II. Synthesis of Poly[octene-*pseudorotaxa*-(alpha-Cyclodextrin)]

CHAPTER 6

INTRODUCTION

6.1 CYCLODEXTRIN-ROTAXANATED POLYMERS

Supramolecular self-assemblies are an intriguing topic in organic and polymer chemistry for purposes ranging in functionality from electronics to bioengineering applications. Polyrotaxanes, especially those formed as cyclodextrin inclusion complexes (ICs), are under particular scrutiny because of the various chemical and physical properties offered by cyclodextrins (CDs). CDs are rigid, cyclic oligomers comprised of 6, 7, or 8 glucose units, and are named α, β, γ-CD, respectively. The exterior of CD is polar and hydrophilic due to the three hydroxyl groups per repeat unit, but the cavity is hydrophobic. Although the depth of the inner CD cavities is the same for all three molecules, the cavity diameters are different: 4.5 Å for α-CD, 7.0 Å for β-CD, and 8.5 Å for γ-CD (see Figure 6.2).[1,2]

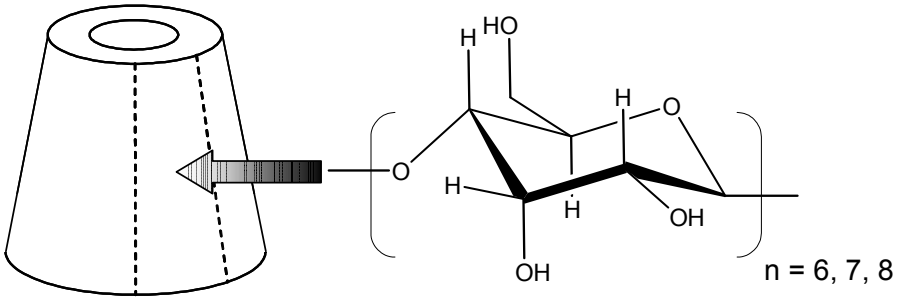
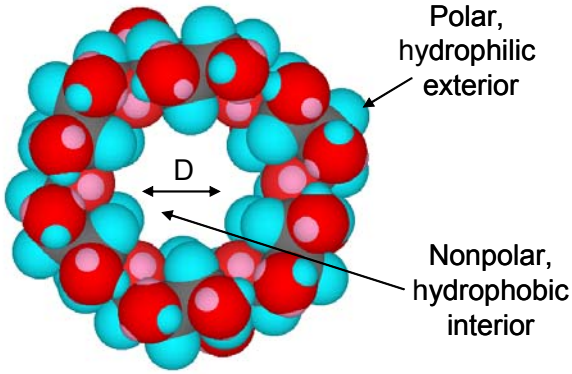


Figure 6.1 – The chemical structure of a single repeat unit for cyclodextrin is shown.

As expected, this trait of varied cavity dimensions has a dramatic effect on the diameter of molecules that can be included by CDs, but no effect is seen with regards to the length of the guest molecule. Short and long molecules (polymers) alike are able to reside within the cavities of their CD hosts.



D_α = 4.5 Å, D_β = 7.0 Å, D_γ = 8.5 Å

Figure 6.2 – The depth of cyclodextrin does not change with respect to the number of repeat units comprising the molecule, but the inner diameter of the cavity is affected.

Several driving forces for CD inclusion complexes with polymers have been observed, including (1) the hydrophopic interactions between the inner cavity of the CD and the polymer, (2) steric compatibility between the host and guest molecules, and (3) intermolecular hydrogen bonding between neighboring CDs threaded onto the same polymer chain.[3-5]

When macromolecules form ICs with CDs, the complex is a channel-type crystal structure that occurs presumably as an effect of the long chain nature of the guest molecule. The guest polymer chains are constrained by the CDs to assume extended conformations along narrow cylindrical channels (~5–10 Å) with no degrees of freedom other than rotational motions along the backbones.[6,7] The host CDs also separate each

polymer chain from neighboring chains and prevent the included polymers from mixing and forming continuous phases (see Figure 6.3).[8]

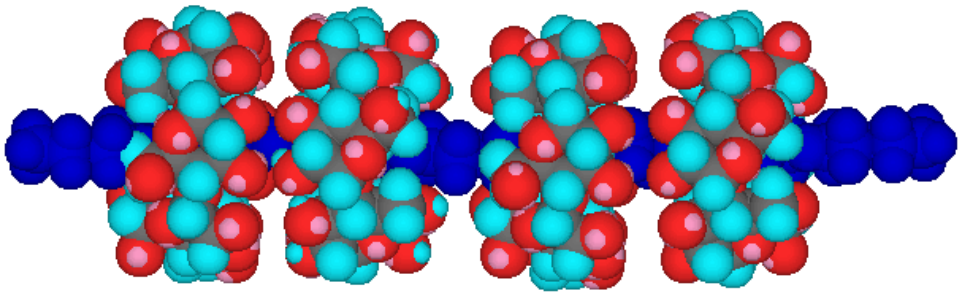


Figure 6.3 – α-CD threads onto the backbone of linear polymer chains and the complexes form a channel-type crystal structure.

Engineering electronic devices at the molecular level takes advantage of this isolation of polymer chains. Polymers with conjugated backbones are capable of being conductive molecular wires, but interchain charge mobility and π-π stacking interactions between the polymer chains are major drawbacks. One method of preventing cross-talk between polymers is insulating them within CD molecules. This method limits inter-chain interactions and enhances the desired one-dimensional nature of the transport properties.[9-11]

ICs formed from polymers and CDs have also been exploited to produce molecular nanotubes of pre-determined dimensions. PEG-*rotaxa*-αCD was prepared with blocking groups on each polymer end to prevent dethreading. The α-CD molecules were then crosslinked with epichlorohydrin, and the blocking groups were removed. PEG dethreaded in solution to yield a nanotube of the desired 4.5 Å diameter.[12,13]

ICs have also been used to overcome polymer miscibility differences to form intimately mixed blends. Poly(L-lactic acid) (PLLA) and poly(ε-caprolactone) (PCL) form an immiscible blend from solution cast methods, but a miscible polymer blend was formed with these two polymers when α-CD ICs of PLLA and PCL were mixed together and then washed with hot water to remove all of the α-CD.[14] This method was also applied to a copolymer system of PLLA-*block*-PCL.[15] Suppression of phase separation led to a decrease in crystallinity and to a much faster enzymatic degradation than that of the as-synthesized copolymer or the solution-cast blends.[16]

A similar procedure was also followed for PCL and poly(propylene glycol) (PPG) triblock copolymers that formed ICs with γ-CD; the copolymer coalesced from its IC crystals with γ-CD to have decreased crystallinity.[17] A blend of poly(R,S-3-hydroxybutyrate) (a-PHB) and PCL formed an IC with γ-CD. The γ-CD was washed away by hot water and the coalesced blend exhibited a single T_g between the T_g's of a-PHB and PCL, while no change in T_g's were seen for the samples prepared as solution-cast physical blends.[18] These results indicate that phase segregation occurred in the samples prepared as solution-cast physical blends, but the polymers are intimately mixed in the blends prepared from ICs.

6.2 INTRODUCTION TO ACYCLIC DIENE METATHESIS (ADMET)

Acyclic diene metathesis (ADMET) is a step-growth polymerization of an α,ω-diene using an organometallic metathesis catalyst to produce polymers which are completely linear, free from chain transfer, branching and other defects, and possess well-defined end groups.[19] High molecular weight unsaturated polymers and copolymers

are synthesized when monomer conversions approach 99%, as is customary for step-growth polymerizations.

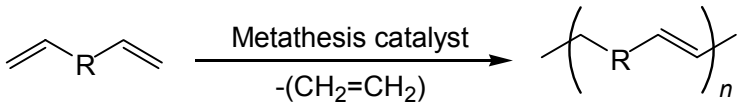


Figure 6.4 – ADMET polymerizations are step-growth in nature that require ethylene to be removed from the system in order to synthesize high molecular weight polymers, which have regularly unsaturated bonds.

As shown in Figure 6.5, all of the steps in the mechanism are in equilibria, therefore the overall polymerization is driven by the removal of a small molecule from the system;[20] in the case of ADMET, ethylene must been removed. A vast array of polymers and copolymers[21-28] have been synthesized including completely hydrocarbon polymers,[19,20,28-30] polyethers,[31-33] polyesters,[34,35] polycarbonates,[36] polycarbosiloxanes,[37] polycarbosilanes,[38-40] polythioethers,[41] and polyalcohols.[28,42]

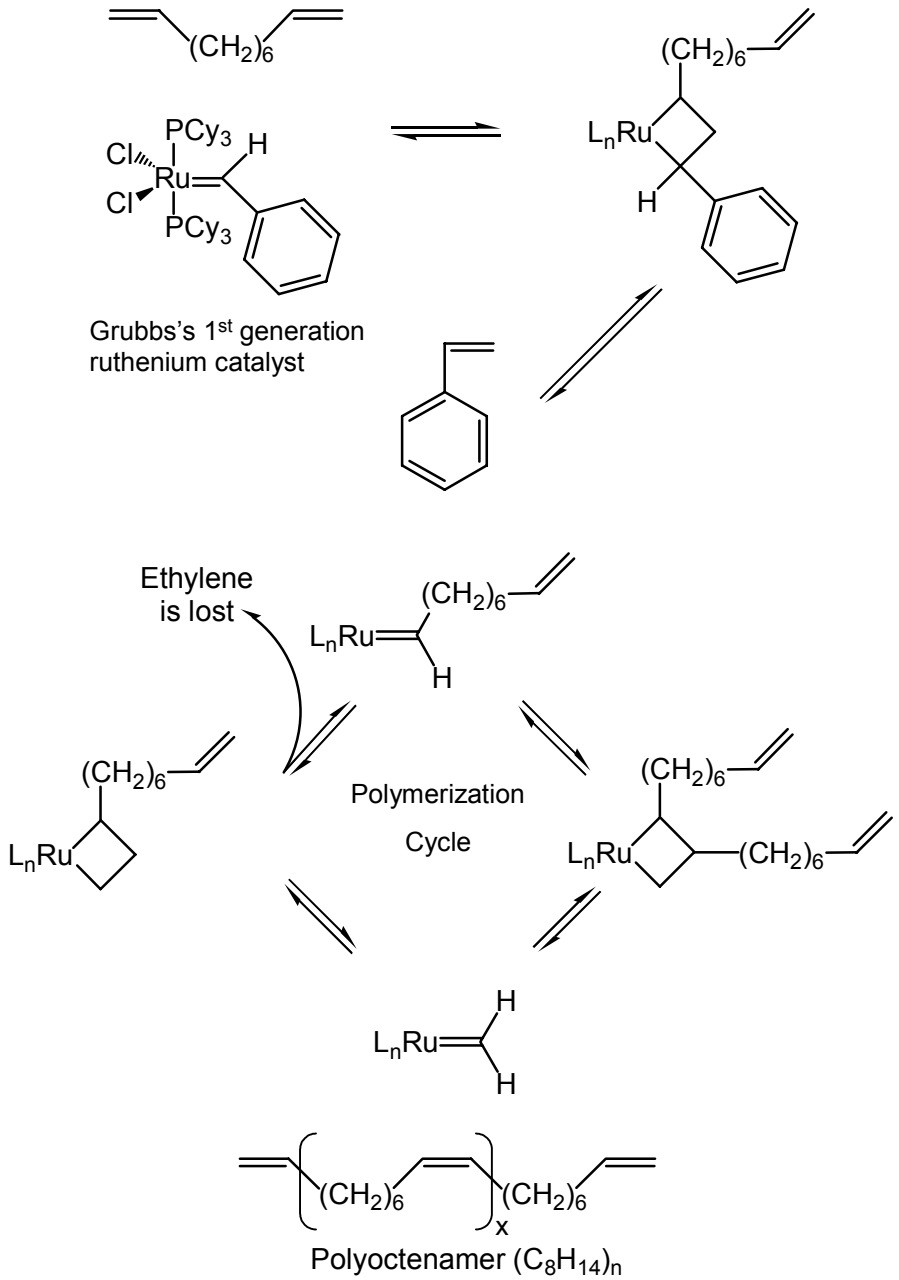


Figure 6.5 – The polymerization mechanism of 1,9-decadiene via ADMET.

Several conditions must be satisfied before ADMET polymerizations are able to proceed. (1) The monomer cannot be restricted by factors that control intramolecular versus intermolecular metathesis;[19] the goal is for reaction to occur between external olefin bonds of different molecules, and this mechanism must not be prevented by steric constraints that cause cyclization instead of polymerization. (2) Methylene spacers are

required to separate the vinyl bond from monomer functionality to prevent coordination of a heteroatom's nonbonded electrons with the metal of the catalyst. This complexation is known as the "negative neighboring group effect"[31,34,36] and prevents the catalyst from maintaining its activity. (3) Methylene spacers are also necessary to separate the olefin end-group from sterically hindering moieties, such as dimethylsilyl groups, that may spatially prevent coordination of the metallocene catalyst to the vinyl bond.[37]

Since ADMET is an equilibrium step-growth reaction of α,ω-dienes, monovinyl compounds act as chain-terminating agents.[43] Not only can this chemistry be exploited to control the molecular weight of the polymer, but it also provides an elegant method of terminating all chain ends with the same end-group. This feature stands in stark contrast to other polymerization techniques. Free radical polymerizations can use a single initiating compound to provide identical end-groups as long as the polymer chain terminates completely by coupling, but few polymers terminate quantitatively coupling. Anionic or cationic polymerizations require an initiator with the appropriate end-group attached *and* either a terminating agent with the appropriate end-group or an agent to couple the growing chains. Utilizing ADMET to provide telechelic polymers is straightforward and does not require monitoring the polymerization in order to determine the appropriate time to add terminating or coupling reagents.

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CHAPTER 7

SYNTHESIS OF END-CAPPED POLYOCTENE BY ADMET

7.1 INTRODUCTION

Polyoctenamer (PO) and end-capped PO (ecPO) were synthesized by ADMET utilizing Grubbs's 1st generation ruthenium catalyst to polymerize 1,9-decadiene in methylene chloride. Ethylene gas was removed from the system by refluxing the solvent under an inert atmosphere. Grubbs's 1st generation ruthenium catalyst was chosen because of its robustness, especially against oxygen, water, and minor solvent impurities.[1] The monovinyl compound, which was used to control the molecular weight of ecPO and provide blocking groups on both ends of the chain to prevent cycles smaller in circumference than forty-two carbon, oxygen, or sulfur atoms from threading onto the polymer backbone, was synthesized through a coupling reaction of *tris*(*p-tert*-butylphenyl)(4-hydroxyphenyl)methane with 5-hexenyldimethylchlorosilane.

7.2 EXPERIMENTAL PROCEDURE

7.2.1 Materials

All reagents were used as received unless otherwise noted. *p-tert*-Butylbromobenzene (98%), Grubbs's 1st generation ruthenium catalyst (97%), hexane (HPLC grade, 95%), heptane (HPLC grade, 99%), hydrochloric acid (ACS grade, 37%), magnesium turnings (98%), methanol (98%), methyl *tert*-butylbenzoate (99%), methylene chloride (anhydrous, 99.8%), phenol (99%), tetrahydrofuran (anhydrous, 99.9%), tetrahydrofuran (HPLC grade, 99%), and toluene (anhydrous, 99.8%) were

purchased from Sigma-Aldrich Co. 1,9-Decadiene (96%) was obtained from Sigma-Aldrich Co. and purified by stirring over CaH_2 overnight followed by distillation under vacuum at room temperature and 500 mTorr. 5-Hexenyldimethylchlorosilane (95%) was purchased from Gelest. Macroporous anion-exchange resin AG MP-1M (1 mequiv/mL, 0.7 g/mL, 100-200 mesh, chloride form) was purchased from Bio-Rad Laboratories and dried under vacuum prior to use. α-CD was used as received from Wacker.

7.2.2 Instrumentation

IR spectroscopy was performed on a Bruker Vector 22. Liquis samples were analyzed on KBr salt plates and solid samples were analyzed by making pellets with KBr. GPC was conducted in THF (1 ml/min) at 303 K on three Waters Styragel columns (5 μm beads: HR 1, 100 Å, HR 3, 1000 Å, HR 4, 10,000 Å) that were connected to a Waters 2690 separations module and Waters 2410 refractive index detector. ^{13}C NMR spectra were measured on a Bruker AMX 400 in $CDCl_3$ at room temperature. ^{1}H NMR spectra were measured on a Bruker DRX 500 in $CDCl_3$ at room temperature. DOSY was conducted on a Bruker DRX-500 spectrometer using 5 mm tubes. Sample concentrations were 0.5% (w/v) in $CDCl_3$. Spectra were constructed by assuming monoexponential diffusion decays for all chemical shifts. DSC measurements were performed under an inert atmosphere at a heating rate of 10 °C/min on a Seiko DSC 220C calibrated with indium. TGA was performed under an inert atmosphere on a Seiko TG/DTA 320 at a heating rate of 10 °C/min.

7.2.3 Synthesis

Glassware was dried at 120 °C overnight; all liquid transfers occurred via gastight syringes unless otherwise noted.

Tris(p-tert-butylphenyl)methanol.

Into an oven-dried 1-L, three-neck flask equipped with stir bar, condenser, and nitrogen inlet were placed magnesium turnings (9.60 g, 0.40 mol) in THF (650 ml). *p-tert*-Butylbromobenzene (44.0 ml, 0.26 mol) in THF (100 ml) was added dropwise via syringe pump over the course of 1 hr with gentle heating. The reaction was stirred for 2 hrs until a brown color was observed. Methyl *tert*-butylbenzoate (23.0 ml, 0.12 mol) in THF (100 ml) was added dropwise via syringe pump over the course of 1 hr. After refluxing overnight, the solution was cooled to room temperature and neutralized with 10% HCl until the mixture became a transparent solution. Product was extracted with heptane (3×150 ml), and the combined organic phases were washed with water (3×300 ml), then dried over magnesium sulfate. A yellow solid was obtained after removing the solvent by rotary evaporation. The product was purified by recrystallizing twice from methanol to yield a white powder (37.86 g, 74 %). ^{1}H-NMR: 1.30 (s, 27H, CH_3), 2.71 (s, 1H, OH), 7.18 (dd, 6H, arom), 7.31 (dd, 6H, arom). ^{13}C-NMR: 31.40, 34.47, 81.55, 124.72, 127.59, 144.26, 149.84

Tris(p-tert-butylphenyl)(4-hydroxyphenyl)methane.

Into an oven-dried 250-ml, three-neck flask equipped with a stir bar, condenser, and nitrogen inlet was added *tris*(*p-tert*-butylphenyl)methanol (24.67 g, 0.057 mol). Phenol (104.0 g, 1.11 mol) was added and the alcohol was dissolved by warming the mixture. Once solution was established, concentrated HCl (2.0 ml, 0.0229 mol) was added as a catalyst. A deep reddish-blue color was observed immediately. After refluxing overnight, the solution was cooled to room temperature. Product was extracted with toluene (3×150 ml), and the combined organic phases were washed with aqueous NaOH solution (3×250 ml), washed with water (3×350 ml), and dried over magnesium sulfate. A white powder (19.40 g, 0.038 moles, 67%) was obtained after recrystallizing twice from a toluene/hexane solution (3:2). ^{1}H-NMR: 1.30 (s, 27H, CH_3), 6.72 (d, 2H, arom), 7.02 (d, 2H, arom), 7.08, 7.22 (2d, 12H, arom).

5-Hexenyldimethyl{4-[tris(p-tert-butylphenyl)methyl]phenoxy}silane (mvBG).

Into an oven-dried 250-ml, three-neck flask equipped with a stir bar, condenser, and argon inlet was added sodium hydride (0.1378 g, 5.74 mmol) under positive argon flow. THF (100 ml) was added via canula, and the mixture was stirred while *tris*(*p-tert*-butylphenyl)(4-hydroxyphenyl)methane (2.5163 g, 4.99 mmol) was added. After stirring the mixture for 1 hr to ensure complete deprotonation, 5-hexenyldimethylchlorosilane (1.20 ml, 6.08 mmol) was added by syringe, and the reaction was refluxed overnight. The milky yellow solution was cooled to room temperature, and AG MP-1M macroporous resin (3.5603 g, 5.09 mmols, 1.0 eq) was added to remove any unreacted, yet charged species.[2] After 1 hr, the mixture was filtered and solvent was removed by

rotary evaporation. The yellow product was purified by precipitating from an acetone (50 ml) solution with methanol (150 ml). A white powder (2.4432 g, 3.79 mmol, 76 %).was obtained after drying the product under vacuum at 70 °C. ^{1}H-NMR: 0.21 (s, 6H, CH_3), 0.69 (t, 2H, CH_2), 1.28 (s, 27H, CH_3), 1.40 (m, 4H, CH_2), 2.02 (q, 2H, CH_2), 4.89 (dd, 2H, CH_2, J = 11.3 Hz, J = 17.4 Hz), 5.74 (m, 1H, CH), 6.65 (dd, 4H, arom, J = 8.8 Hz, J = 118.8 Hz), 7.04 (dd, 12H, arom, J = 8.8 Hz, J = 56 Hz).

Polyoctenamer (PO).

Into a one-necked, 10-ml flask equipped with a stir bar, condenser, and gooseneck was added a degassed solution of 1,9-decadiene (1.00 ml, 0.86 mmol) in methylene chloride (5.00 ml). Grubbs's 1st generation catalyst (0.0076 g, 0.0093 mmol) was added to the solution and bubbling commenced as ethylene gas was released. The pink solution was refluxed overnight. After 16 h, the solution was cooled to room temperature and added dropwise into methanol (100 ml). The brown product was filtered, dissolved in methylene chloride (10 ml), and added to THF (100 ml). Methanol (150 ml) was added via pipet until the white polymer precipitated from solution. Polyoctenamer was filtered and dried in vacuo. ^{1}H-NMR: 1.40 (br, 8H, CH_2), 2.05 (br, 4H, CH_2), 5.44 (br, 2H, CH).

End-capped Polyoctene (ecPO).

Into an oven-dried 15-ml test tube were placed mvBG (0.3185 g, 0.494 mmol), 1,9-decadiene (0.50 ml, 2.73 mmol) and methylene chloride (5.0 ml). The solution was subjected to three cycles of freeze-pump-thaw to remove dissolved oxygen and then warmed to room temperature. A one-necked, 10-ml flask with stir bar was fitted with a

rubber septum, and the monomer solution was transferred by syringe. Grubbs's 1st generation catalyst (0.0098 g, 0.012 mmol) was added under positive argon flow. Bubbling commenced indicating the evolution of ethylene gas. When bubbling had subsided, a condenser and Teflon-valved-gooseneck were placed onto the one-necked, 10-ml flask reaction flask. After attaching the apparatus to an argon line and refluxing the solution for 72 hours, the solution was cooled to room temperature and the polymer was precipitated into methanol. ecPO was collected as a white powder (0.45643 g, Yield = 67%). To ensure all ends of the polymer were end-capped, the polymer (0.202 g, 0.078 mmol) and mvBG (0.500 g, 0.078 mmol) were placed in a two-necked, 15-ml flask equipped with a stir bar, condenser, and gooseneck. Methylene chloride (10 ml) was transferred via syringe followed by the addition of Grubbs's 1st generation catalyst (0.0139 g, 0.0169 mmol). The solution was refluxed overnight, cooled to room temperature, and the polymer precipitated into methanol. ^{1}H-NMR: 0.21 (s, 6H, CH_3), 1.40 (br, 496H, CH_2), 2.05 (br, 268H, CH_2), 5.44 (br, 124H, CH), 6.65 (dd, 4H, arom, J = 8.8 Hz, J = 118.8 Hz), 7.04 (dd, 12H, arom, J = 8.8 Hz, J = 56 Hz).

7.3 RESULTS AND DISCUSSION

7.3.1 Synthesis of PO and ecPO

ADMET chemistry is a step-growth polymerization of an α,ω-diene using an organometallic metathesis catalyst. PO has previously been reported as being synthesized by ADMET to sufficiently high molecular weight such that external olefin bonds were unnoticeable by IR spectroscopy.[3] Furthermore, mono-vinyl monomers have been shown to control the molecular weight of ADMET-produced polymers by acting as

chain-terminating agents,[4] so this chemistry was exploited to provide PO and ecPO. 1,9-Decadiene was polymerized in methylene chloride by Grubbs's 1st generation catalyst in the presence of mvBG to produce an end-capped polymer, which was unthreadable by cycles smaller in circumference than forty-two carbon, oxygen, or sulfur atoms. The *tris*(*p-tert*-butylphenyl)methyl unit was chosen because it has been shown to be too large for cyclic molecules smaller than 42-crown-14 to pass over it.[5-7]

The end-capping moiety was synthesized as shown in Figure 7.1 by refluxing two equivalents of *p-tert*-butylbromobenzene in the presence of methyl *tert*-butylbenzoate and magnesium turnings to produce *tris*(*p-tert*-butylphenyl)methanol via a Grignard reaction. This was followed by taking advantage of the susceptibility of *tris*(*p-tert*-butylphenyl)methanol to form a stable carbocation at the tertiary carbon under acidic conditions. An electrophilic aromatic substitution reaction was performed by refluxing phenol in the presence of *tris*(*p-tert*-butylphenyl)methanol and concentrated HCl.[8] Finally, t*ris(p-tert*-butylphenyl)(4-hydroxyphenyl)methane was deprotonated by sodium hydride and reacted with 5-hexenyldimethylchlorosilane. Overall, the vinyl-terminated blocking group, hexenyldimethyl{4-[*tris*-(4-*tert*-butylphenyl)methyl]phenoxy}silane, was synthesized in 40% yield.

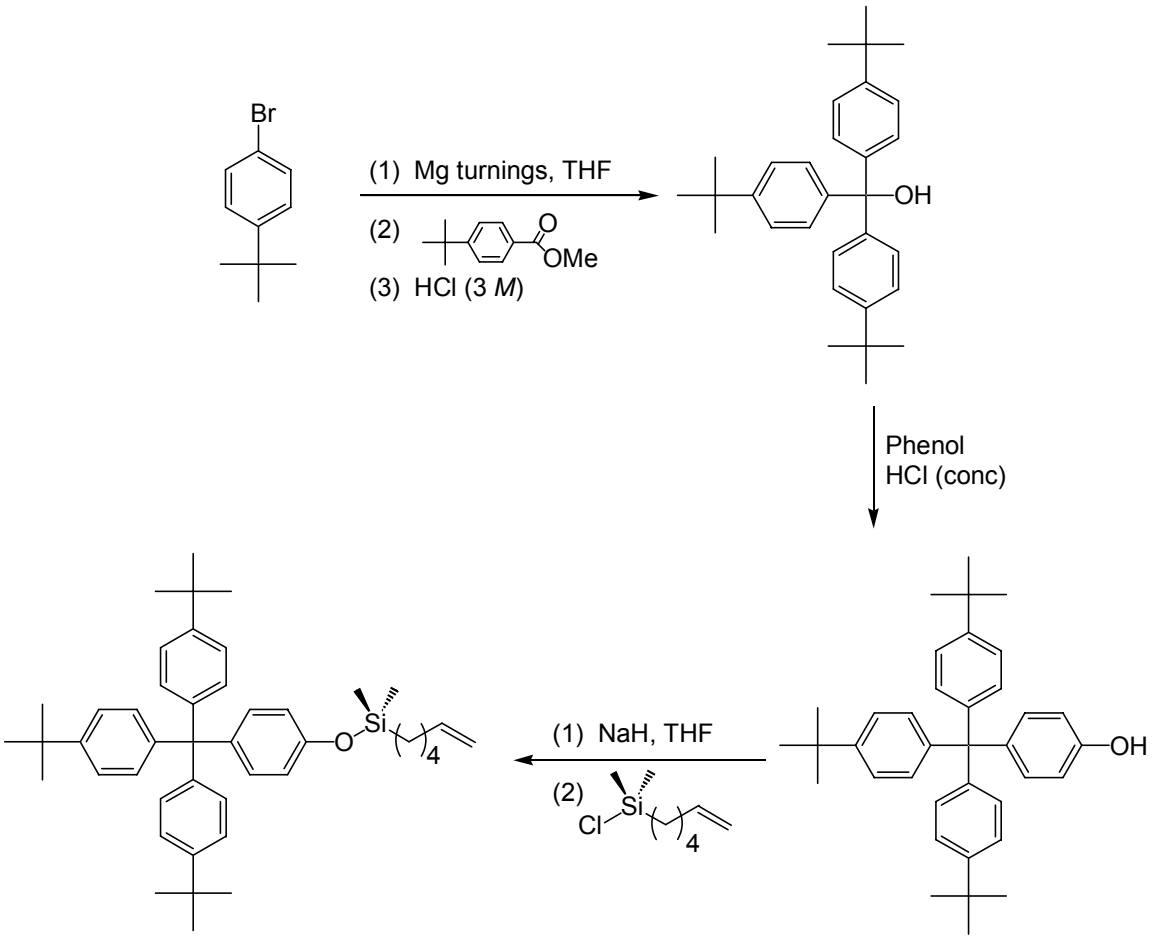

Figure 7.1 – Synthesis of the mono-vinyl blocking group (mvBG) utilized as an end-capping agent.

The molecular weight of ecPO was controlled by the amount of the end-capping agent added to the polymerization solution (see Figure 7.2). The expected molecular weight of ecPO was 2,500 g/mol based on the monomer:mvBG ratio. GPC determined M_n = 3,300 g/mol (PDI = 1.4) based on polystyrene standards, and ^{1}H NMR determined M_n = 2,600 g/mol. To ensure that all ends of the polymer chains were terminated with blocking groups, ecPO was refluxed in a methylene chloride solution of Grubbs's 1st generation catalyst and mvBG; no change in molecular weight was observed by GPC or ^{1}H NMR.

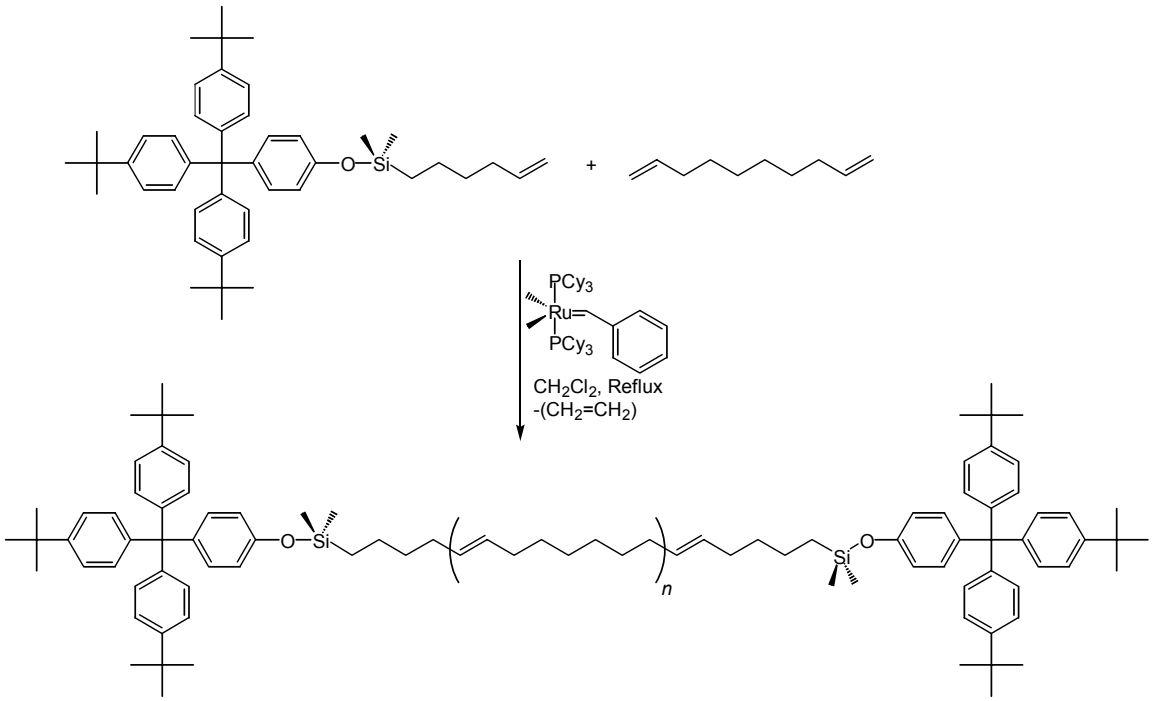

Figure 7.2 – Synthesis of ecPO by ADMET utilizing mvBG to control the molecular weight through chain termination and to prepare a polymer unthreadable by α-CD.

7.3.2 Spectroscopic Characterization of PO and ecPO

IR and ^{1}H NMR demonstrated the conversion of external olefin bonds of 1,9-decadiene and mvBG to internal olefin bonds of PO. In Figure 7.3 demonstrating a comparison of IR spectra for 1,9-decadiene, mvBG, PO, and ecPO, the peak at 1639 cm^{-1} representing the external vinyl bond for 1,9-decadiene has disappeared in the spectra for the polymers. Peaks present in the PO spectrum at 964 cm^{-1} and 714 cm^{-1} are indicative of *trans*-alkene and *cis*-alkene bonds, respectively, and demonstrate that the internal olefin bonds within the polymer are primarily *trans*-alkene. As expected, the spectrum for ecPO looks like an overlay of PO and mvBG minus the peak for an external olefin bond.

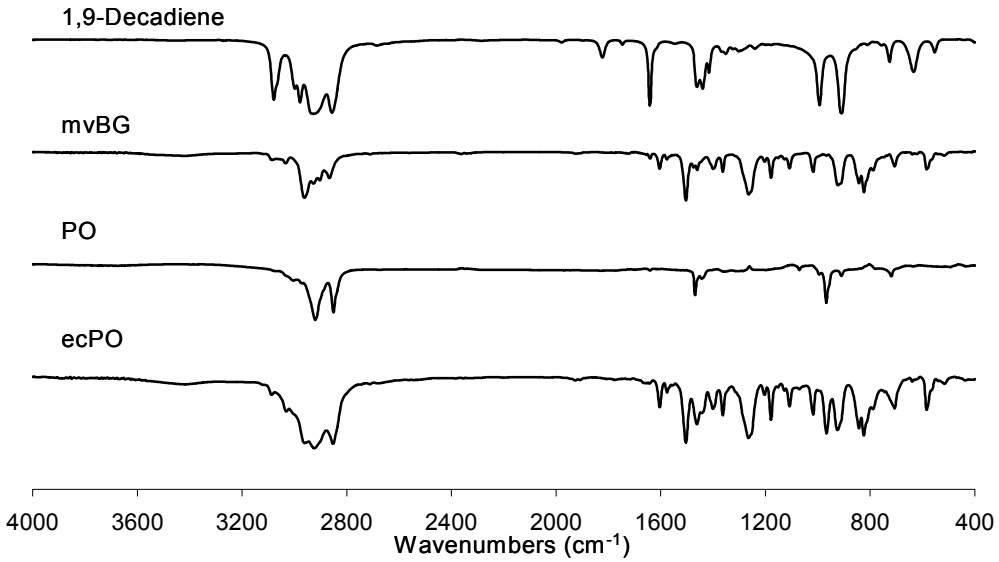

Figure 7.3 – IR spectra detailing the conversion of 1,9-decadiene and mvBG to PO and ecPO. The peak at 1639 cm^{-1} representing the external vinyl bond for 1,9-decadiene has completely disappeared in the spectra for the polymers.

^{1}H NMR clearly shows the conversion of the external vinyl protons at 4.9 ppm and 5.8 ppm of mvBG to internal vinyl protons at 5.4 ppm of ecPO. The peaks for ecPO are also quite broad, which is common in the ^{1}H NMR of polymers. As shown in Figure 7.4, peaks for mvBG are found in the aromatic region, at 4.9 and 5.8 ppm for the external vinyl bond, over the range from 0.7–2.8 ppm for the aliphatic chain, and at 0.2 ppm representing the silyl methyl protons. Peaks within the aromatic region and representing the silyl methyl protons are resolved from peaks of the PO polymer backbone and can therefore be used to determine the number-average molecular weight. Specifically, the molecular weight of ecPO was determined by normalizing the integration values of the silyl methyl protons and comparing to normalized integration values for the internal olefin protons. Examining any normalized integration values for the end-groups and

comparing to any normalized integration values of the polymer backbone resulted in almost identical molecular weight averages.

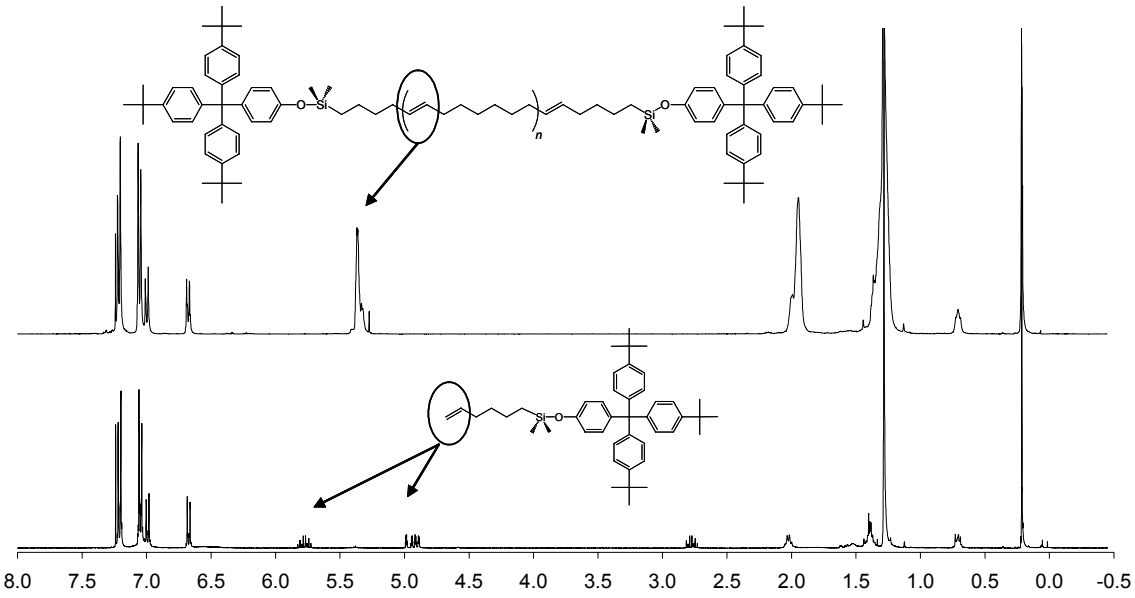

Figure 7.4 – NMR spectra of mvBG and ecPO demonstrating the disappearance of external vinyl protons represented at 5.0 ppm and 5.8 ppm of mvBG and the formation of internal vinyl protons seen at 5.4 ppm.

Two-dimensional diffusion-ordered NMR spectroscopy (DOSY) was used to correlate diffusion coefficients with molecular structure via chemical shifts as previously described in studies regarding poly(ethylene glycol-*rotaxa*-αCD)[9] and polystyrene-*rotaxa*-(30-crown-10).[10] When two or more molecules are present in dilute solution, each molecule diffuses at a rate proportional to its molecular weight; smaller molecules diffuse faster than larger molecules. DOSY is capable of resolving different diffusion rates present within a solution, which provides evidence for the number of molecular species present in solution. As Figure 7.5 shows, three molecules are present in the NMR sample solution: water [δ 1.5 ppm, log (D/m^2s^{-1}) = -8.6], $CHCl_3$ [δ 7.24 ppm, log (D/m^2s^{-1}) = -9.1], and ecPO [log (D/m^2s^{-1}) = -10.2]. The plot demonstrated that the aromatic protons

(6.6–7.2 ppm) and silylmethyl protons (0.2 ppm) for the end-capping agent diffuse in dilute solution at the same rate as the protons within the polymer backbone.

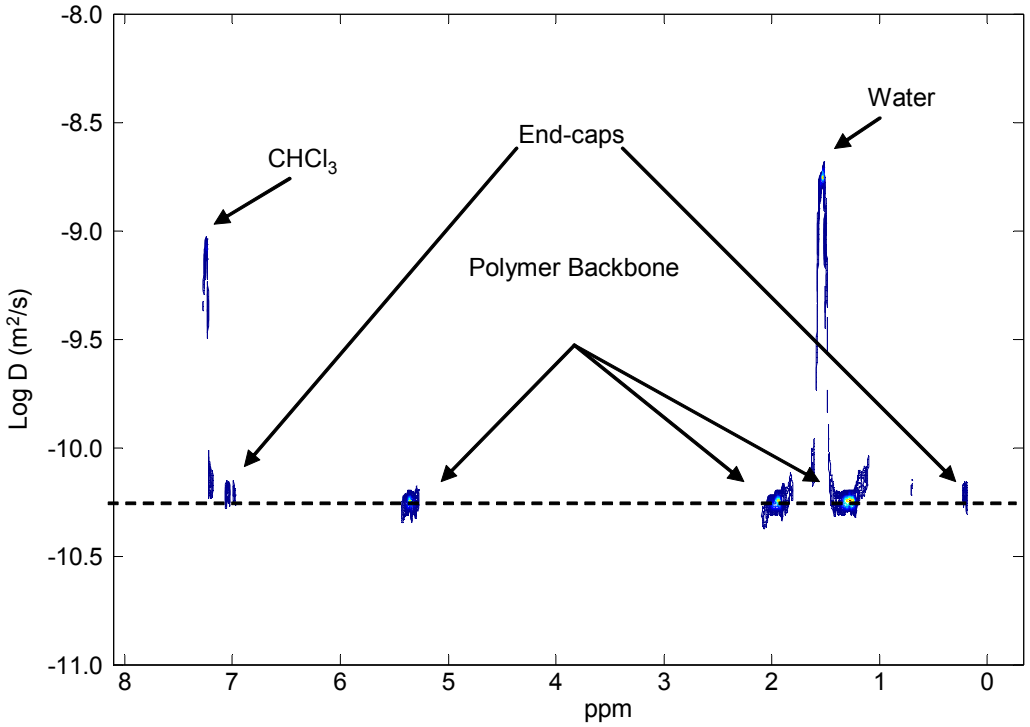

Figure 7.5 – DOSY plot of log (D/m^2s^{-1}) versus chemical shift for ecPO. A single self-diffusion coefficient is apparent for the polymer and the end-groups lending support that all of the blocking groups present in solution are attached to polymer chains.

^{13}C NMR was used to corroborate the structure of ecPO, but this technique was also used to determine the stereochemistry of *trans*- versus *cis*- along the backbone.[11,12] IR has been utilized in this regard as well,[11] but overlapping peaks from the end-capping agent prevented that analysis. Proof of structure lies in the fact that all resonances were assigned, and the polymer appeared to be 84% trans. The peak intensity of the *trans* olefin carbon found at 130.4 ppm was compared to the peak intensity of the *cis* olefin carbon found at 129.8 ppm. This direct comparison of peak height allows the

determination of stereochemistry along the polymer backbone. The same information can be gathered by comparing the peak heights of carbons adjacent to *cis* olefin bonds (27.3 ppm) versus the peak heights of carbons adjacent to *trans* olefin bonds (32.7 ppm).[11-13]

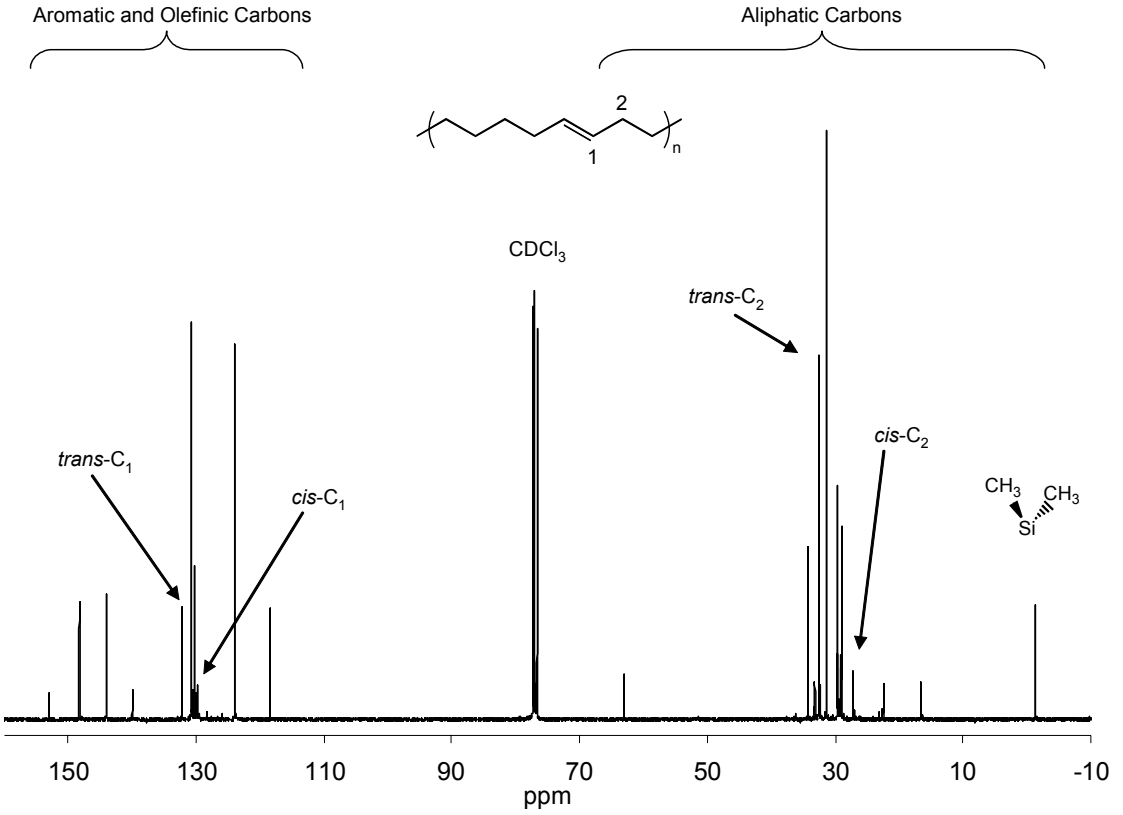

Figure 7.6 – ^{13}C NMR spectrum of ecPO. By comparing peak heights at 129.8 ppm for *cis*- and 130.4 ppm for *trans*-internal olefinic carbons, the polymer was found to be 84% *trans*.

7.3.3 Thermal Characterization of PO and ecPO

An expected effect on the thermal behavior of PO by the bulky end-capping agents is a decrease in melting and crystallizing temperatures because the bulky groups should disrupt the crystal structure of the PO. This is indeed the case. Melting and crystallizing temperatures of PO are linearly related to the *trans* content. The solid black

points in Figure 7.7 display data, which was published for PO containing various amount of %-*trans* content.[11] The solid black lines are best-fit lines that demonstrate the linear relationship. The %-*trans* content within the ecPO backbone was determined by ^{13}C NMR as previously discussed, then the polymer was analyzed by DSC to determine T_m and T_{rc}. The transition temperatures for ecPO are shown in the figure as white data points, and demonstrate that the bulky end groups decreased the expected T_m by 13 °C and T_{cr} by 10 °C. The effect of the end groups should decrease as the molecular weight of the polymer increases.

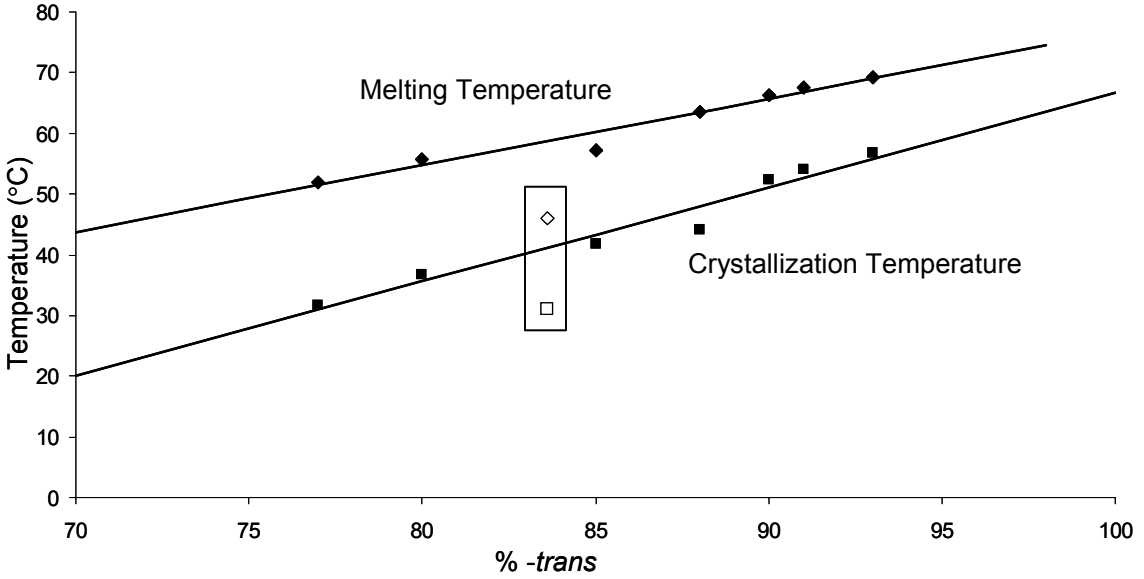

Figure 7.7 – DSC was able to confirm that the bulky blocking groups of ecPO decreased the expected T_m by 13 °C and T_{rc} by 10 °C.

7.4 CONCLUSIONS

PO and ecPO were synthesized by ADMET chemistry using Grubbs's 1st generation catalyst in a refluxing solution of methylene chloride, and the molecular weight of ecPO was controlled by the addition of a chain-terminating reagent. IR and ^{1}H

NMR were used to monitor the conversion of external olefin bonds of the monomers to internal olefin bonds of the PO and ecPO. The peak at 1639 cm^{-1} for the external vinyl bond in the monomer IR spectrum completely disappeared in the spectra for the polymers. ^{1}H NMR showed the disappearance of peaks representing mvBG at 5.0 ppm and 5.8 ppm, while also exhibiting a broad peak at 5.4 ppm for the internal olefin bonds of ecPO; DOSY suggested that the blocking-groups were in fact attached to the polymer chains. The %-*trans* content of ecPO was determined by ^{13}C NMR to be 84%, and the effect on the thermal behavior of the bulky end-groups according to DSC showed a decrease of 13 °C and 10 °C in the T_m and T_{cr}, respectively.

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CHAPTER 8

PRECIPITATES FORMED FROM αCD-SATURATED AQUEOUS SOLUTIONS WITH PO, ECPO, 1,9-DECADIENE, AND THF

8.1 INTRODUCTION

Recently published literature described unexpected results of α-CD forming polypseudorotaxanes with triblock copolymers, which were previously thought to be unthreadable for steric reasons. Triblock copolymers of poly(propylene oxide) with poly(ethylene oxide), PPO-PEO-PPO,[1] and poly(L-lactide) with PEO, PLLA-PEO-PLLA,[2] formed ICs with α-CD even though PPO and PLLA were thought to have too large of a cross-sectional diameter to fit through the cavity of α-CD.[3-7]

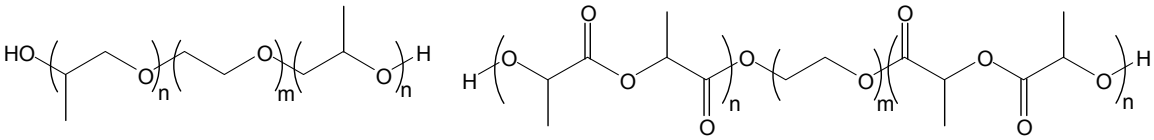

Figure 8.1 – Chemical structures for triblock copolymers described as forming α-CD ICs. Note the ends of the polymers have methyl groups that were thought to prevent inclusion within an α-CD cavity.

These results were surprising, so the experimental methods used to form the ICs were examined to determine if other explanations existed for the results that were seen. PPO–PEO–PPO triblock was added to a saturated α-CD aqueous solution, which was sonicated until the clear solution became turbid. The mixture was allowed to stand for several hours and the precipitate was filtered.[1] Though this procedure was an accepted protocol, the result raised questions as to the effect of sonication on a saturated aqueous

solution of α-CD while in the presence of a possible coalescence agent. Did sonicating a saturated aqueous solution of α-CD in the presence of a 'seeding' agent merely cause α-CD to precipitate on top of the polymer to form a blend instead of an IC? A polymer end-capped with bulky blocking groups to prevent threading by α-CD, ecPO, was subjected to the previously described procedure to determine whether or not the mere presence of a polymer in a saturated aqueous solution of α-CD being sonicated was enough to produce precipitation. The final product was compared to precipitates formed from PO and 1,9-decadiene in α-CD saturated aqueous solutions, which had undergone identical processes.

Several ICs have been formed by dissolving a polymer in an organic solvent, and then pouring this solution into a saturated aqueous solution of CD.[2,8] The samples were sonicated until the clear solutions became turbid, and the mixtures were allowed to stand for several hours before the precipitate was filtered. One example described an intimately compatible blend formed by dissolving PLLA and PCL in 200 ml of dioxane and adding this solution to α-CD dissolved in 50 ml of water.[8] In another case a triblock copolymer of PLLA–PEO–PLLA was dissolved in dioxane or dioxane/acetone before the organic solution was added to the aqueous α-CD solution.[2] One of our aims was to identify any possible effects of the addition of an organic solvent that might itself form an inclusion complex with α-CD. Therefore, THF was added to an aqueous solution of α-CD and the white precipitate was examined.

8.2 EXPERIMENTAL PROCEDURE

8.2.1 Materials

All reagents were used as received unless otherwise noted. Tetrahydrofuran (HPLC grade, 99%), was purchased from Sigma-Aldrich Co. α-CD was used as received from Wacker. 1,9-Decadiene (96%) was obtained from Sigma-Aldrich Co. and purified by stirring over CaH_2 overnight followed by distillation under vacuum at room temperature and 500 mTorr. PO and ecPO were synthesized as previously described.

8.2.2 Instrumentation

IR spectroscopy was performed on a Bruker Vector 22 by making pellets with KBr. Solid-state ^{13}C NMR data were collected using a Bruker DSX-300 spectrometer equipped with a Bruker double-resonance MAS probehead. Standard cross-polarization (CP) with high-powered ^{1}H dipole decoupling was used with ^{1}H and ^{13}C pulses of 4.5 μs. Recycle delays of 4 s and sample spinning speeds of 5 kHz were employed. X-ray diffraction was carried out on a Rigaku MicroMAX WAXD/SAXS system, operating at 45 KV and 0.66 mÅ. Cu Kα 1 irradiation was obtained using a monochromator, and samples were prepared by packing the material into a glass capillary tube and mounting the tube vertically. DSC measurements were performed under an inert atmosphere at a heating rate of 10 °C/min on a Seiko DSC 220C calibrated with indium. TGA was performed under an inert atmosphere on a Seiko TG/DTA 320 at a heating rate of 10 °C/min.

8.2.3 Preparation of Inclusion Complexes

General procedure for the preparation of ICs – IC: PO/α-CD

α-CD (1.52018 g) was dissolved in distilled water (10 ml) by stirring at 60 °C. PO (0.11312 g) was added and the mixture was sonicated for 3 h. A white precipitate formed, and the mixture was cooled to room temperature overnight. After 16 h, the mixture was filtered and dried under vacuum to yield a white powder (0.18676 g, Yield = 12.3%).

Blend: ecPO/α-CD

α-CD (2.15058 g), ecPO (0.07522 g). The mixture was filtered and dried under vacuum to quantitatively yield ecPO.

IC: 1,9-Decadiene/α-CD

α-CD (2.05265 g), 1,9-decadiene (0.25 ml), Yield = 1.83815 g (89.6%).

IC: THF/α-CD

α-CD (2.69125 g), THF (0.50 ml), Yield = 0.60545 g (22.5%).

Blend: ecPO/α-CD from THF

α-CD (0.7906 g) was dissolved in distilled water (4 ml) by stirring at 60 °C. ecPO (0.03929 g) was dissolved in THF (8 ml) and this solution was heated to 60 °C. The polymer solution was added dropwise to the α-CD solution. After stirring for 3 h at

60 °C, the solution was cooled to room temperature overnight. A white solid was filtered from the mixture and washed with THF to remove free ecPO and with cold distilled water to remove free α-CD.

Attempt toward PO-rotaxa-αCD.

Into a 1-necked, 5-ml flask equipped with a stir, condenser, and gooseneck, were added PO/α-CD IC (0.0787 g), mvBG (0.1070 g, 0.166 mmol), and Grubbs's 1st generation ruthenium catalyst (0.0103 g, 0.012 mmol) in methylene chloride (1.0 ml). The suspension was refluxed overnight. The reaction was cooled to room temperature and the polymer was precipitated into methanol (100 ml). The product was filtered, washed with distilled water (50 ml), and dried under vacuum for two hours to yield 0.0732 g of a white solid (93.1%). The solid was not entirely soluble in various solvents, which varied in polarity: dimethylsulfoxide, THF, chloroform, and hexane. From the solubility tests a blend of PO and a-CD seemed to exist, so the product (0.03173 g) was placed in a test tube with hot distilled water (10 ml) and sonicated for 30 minutes to remove free α-CD. The product was filtered and suspended in methylene chloride (10 ml) and sonicated for 30 minutes until a clear solution formed.

Attempt toward 1,9-decadiene-rotaxa-αCD.

Into a 1-necked, 10-ml flask equipped with a stir, condenser, and gooseneck, were added IC: 1.9-Decadiene/α-CD (0.2849 g), mvBG (0.3507 g, 0.544 mmol), and Grubbs's 1st generation ruthenium catalyst (0.0098 g, 0.012 mmol) in methylene chloride (5.0 ml). The suspension was refluxed for 24 h, cooled to room temperature, and second dose of

Grubbs's catalyst was added. The suspension was refluxed for another 72 h. The reaction was cooled to room temperature and the mixture was added dropwise to THF (100 ml). The solids were filtered, dried under vacuum, and analyzed. To the THF solution, methanol (200 ml) was added, but no precipitate formed. Solvents were removed by rotary evaporation. The solids were dried under vacuum and analyzed.

8.3 RESULTS AND DISCUSSION

8.3.1 Inclusion-complexation with α-CD

PO and ecPO, which are insoluble in water, were ground into fine powders and sprinkled into a test tube containing a saturated solution of α-CD in water. The mixtures were sonicated at room temperature for three hours, after which time the mixtures were filtered. Upon examination of the mixtures after sonication, it was immediately clear that ecPO had not formed an inclusion complex. The off-white flecks of polymer remained floating in the aqueous solution and the mass of the vacuum-dried precipitate equaled the initial mass of polymer added to the aqueous solution. This procedure was also followed for the addition of 1,9-decadiene to an α-CD solution. Both PO and 1,9-decadiene yielded a crystalline white solid with α-CD that totaled greater mass than the initial mass of guest molecules added to each solution.

A second experimental procedure involved dissolving ecPO in THF and then adding this solution to a solution of α-CD in water. A white crystalline precipitate formed. This precipitate was washed by THF to remove uncomplexed ecPO and then washed with water to remove free α-CD. The entire amount of the white solid was dissolved during the washing procedures to indicate no threading took place. To examine

the effect of an organic solvent on the precipitation process, THF was added to an aqueous solution of α-CD. The product was not washed for fear of dissolving the entire sample. All precipitates were filtered, dried *in vacuo*, and further examined.

8.3.2 ^{13}C CP/MAS NMR

The ICs were analyzed by IR, but the spectra only revealed the presence of α-CD because these peaks overlapped with peaks of the included molecules. Valuable information was gained, though, when the ICs were analyzed by solid-state ^{13}C CP/MAS NMR. Peaks demonstrating the presence of α-CD were seen over the range 55-102 ppm. In addition to these peaks, which were present in all of the spectra, the resonances for the included molecules were also observed: 1,9-decadiene {29.5 ppm (–**C**H_2–), 33.6 ppm (CH_2=CH–**C**H_2–), 111.7 ppm (**C**H_2=CH–), 139.3 ppm (CH_2=**C**H–)}, PO {26.2-37.4 ppm (–**C**H_2–), 127.3-131.3 ppm (–**C**H=**C**H–)}, and THF {25.0 ppm (–**C**H_2–), 66.7 ppm (–O–**C**H_2–)}, yielding evidence that the guest molecules were present.

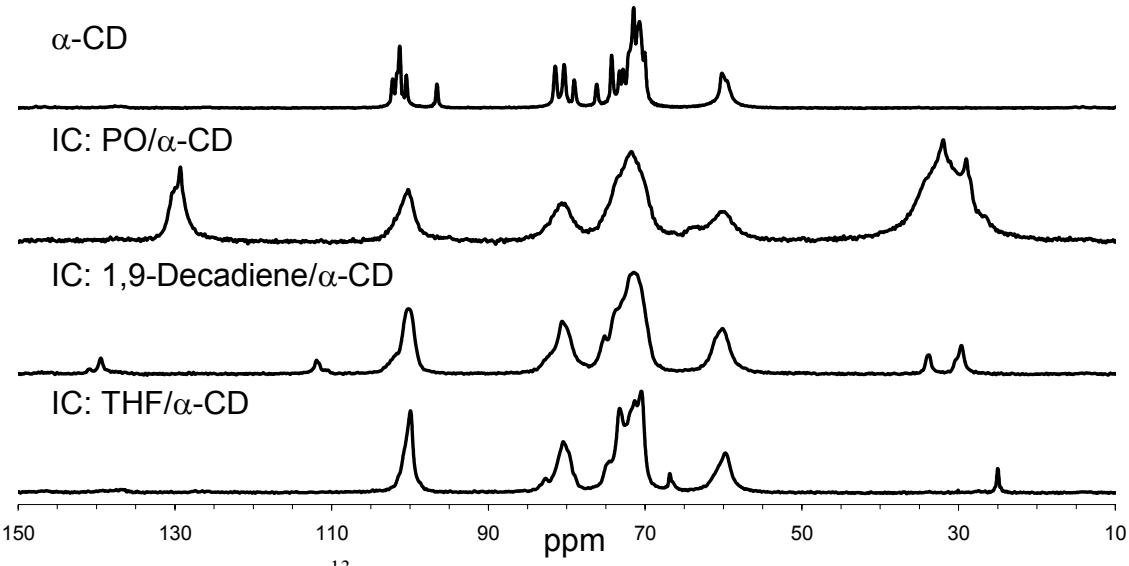

Figure 8.2 – Solid-state ^{13}C CP/MAS NMR spectra of α-CD, and inclusion complexes formed from PO, 1,9-decadiene, and THF, respectively.

The spectrum of α-CD in the uncomplexed state showed strong splitting for all of the $C_{1\text{-}6}$ resonances, such that each carbon of the glucose repeat unit was observed as a single peak. This suggested that α-CD assumed a less symmetrical conformation in the crystalline uncomplexed state,[9] which was supported by X-ray studies of single crystals demonstrating that when α-CD did not include guests in the cavity, a less symmetrical conformation was assumed.[10,11] On the other hand, all $C_{1\text{-}6}$ resonances of complexed α-CD showed less splitting and more unresolved resonances. In addition, the peaks at 76.0 and 96.5 ppm, which represented C_4 and C_1 resonances, respectively, disappeared in the spectra for the ICs. These data indicated that α-CD adopted a more symmetrical conformation and each glucose repeat unit was in a similar environment in the IC. Similar observations, which were believed to support the formation of ICs between CDs and polymers, previously had been observed in the solid-state ^{13}C CP/MAS NMR spectra of various crystalline ICs.[9]

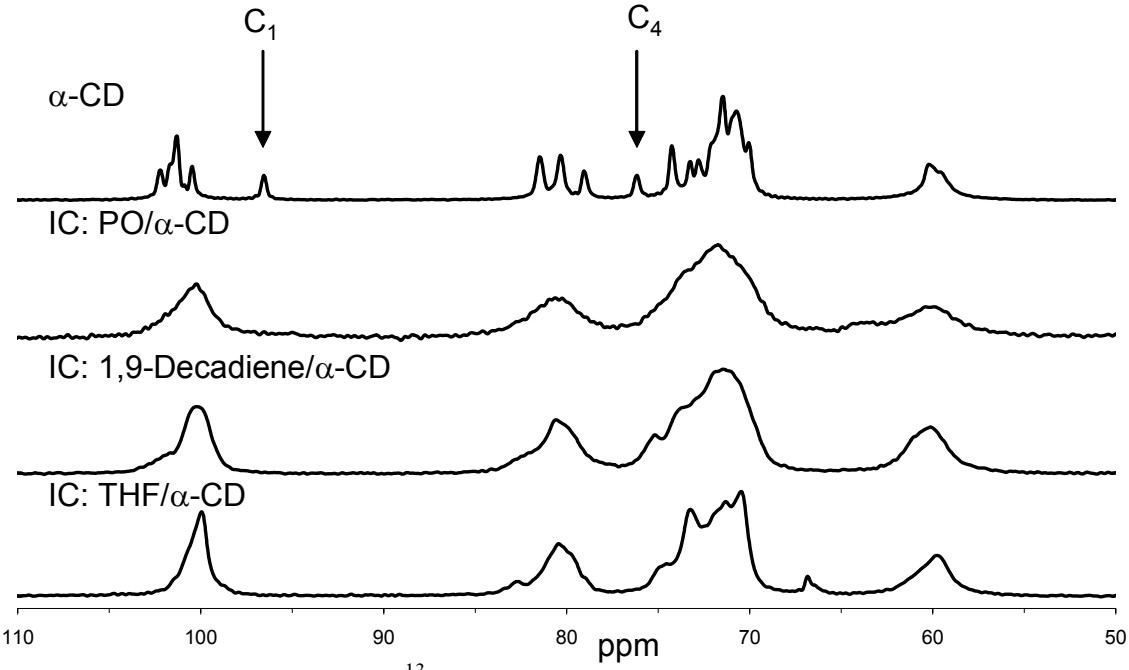

Figure 8.3 – The solid-state ^{13}C CP/MAS NMR spectra of α-CD, and inclusion complexes formed from PO, 1,9-decadiene, and THF, respectively. This view highlights the contrast between the well-defined peaks of crystalline α-CD. Peaks for the inclusion complexes broadened significantly, and the peaks at 76.0 and 96.5 ppm disappeared completely. This information indicated that α-CD adopted a more symmetric cyclic conformation and each glucose unit was in a similar environment.[9]

8.3.3 Wide-angle X-ray Diffraction (WAXD)

The WAXD pattern of pure PO shows diffraction peaks at $2\theta = 21.1°$ and 24.6°, and the diffraction pattern from the PO/α-CD IC was quite obviously not a superposition of the IC components. It was worth noting that the diffraction patterns for the inclusion complexes formed from 1,9-decadiene, PO, and THF, were all quite similar, and the diffraction patterns were nearly identical to those reported for PEG/α-CD,[2,12,13] which was widely accepted as being capable of forming ICs with α-CD. Most interesting,

though, the diffraction patterns also were nearly identical those reported for PLLA/α-CD and PLLA–PEO–PLLA/α-CD,[2] which were prepared from organic solvents.

The specific peaks, which described the crystal structure of α-CD, were present at 2θ = 7.7° (d = 11.5 Å), 13.3° (d = 6.7 Å) and 20.2° (d = 4.4 Å), and were explained by a hexagonal unit cell with lateral dimension a = 13.6 Å.[14] These peaks were present in all of the ICs and indicative of channel structures of α-CD. These peaks were not present in the diffraction pattern for pure α-CD because pure α-CD adopts a cage structure morphology.

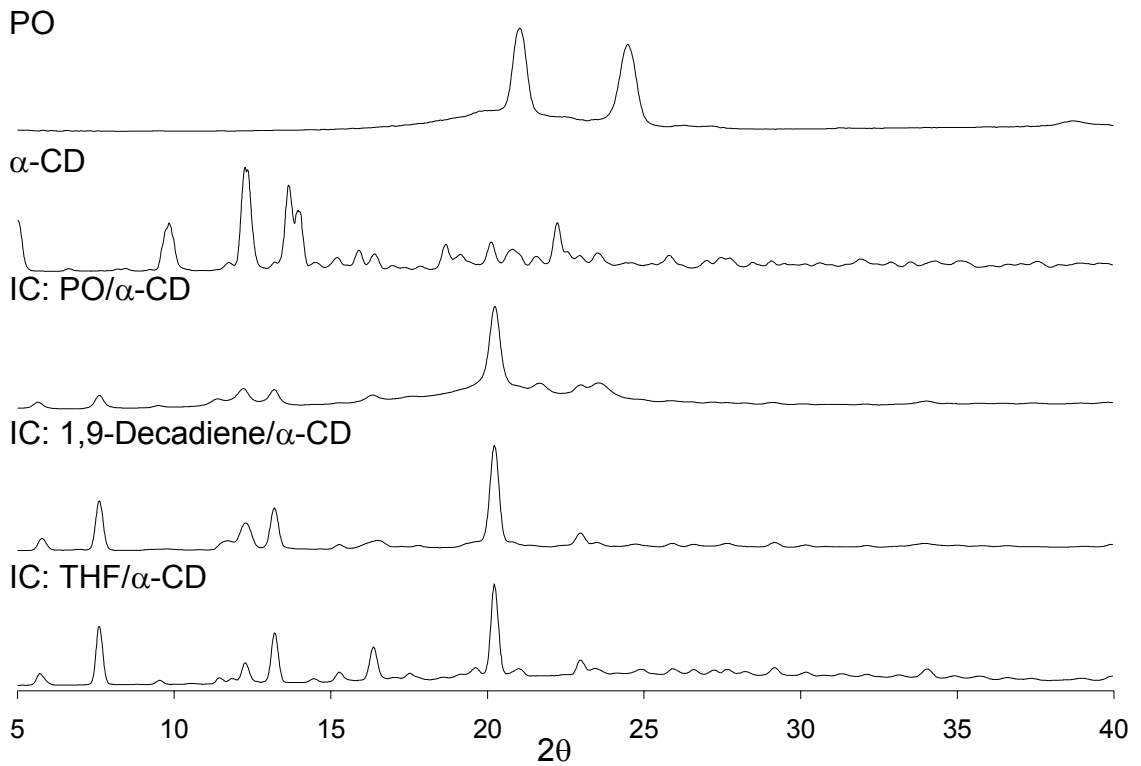

Figure 8.4 – WAXD patterns for PO, α-CD, and ICs formed from 1,9-decadiene, PO, and THF. Peaks for the inclusion complexes at 2θ = 7.7° (11.5 Å), 13.3° (d = 6.7 Å), and 20.2° (4.4 Å) are indicative of channel structures versus cage structures.[2,14]

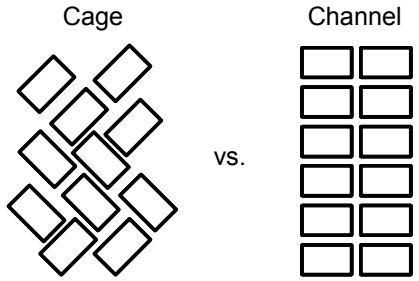

Figure 8.5 – Cage structure morphology for α-CD versus the channel structure expected from polymer/α-CD ICs.

8.3.4 Differential Scanning Calorimetry (DSC)

DSC was another technique that offered evidence of individual polymers chains being included by CDs. When polymers were completely covered by CDs, the chains were segregated from one another and unable to form a continuous phase; DSC thermograms of ICs showed no T_m or T_g transition peaks.[15] In the thermogram for pure PO, a clear T_m was noticeable at 55 °C. The PO/α-CD also exhibited a T_m (50 °C), however, the transition was depressed in temperature and magnitude. This suggested that α-CD prohibited some of the chains from segregating, but did not completely encompass all of the PO.

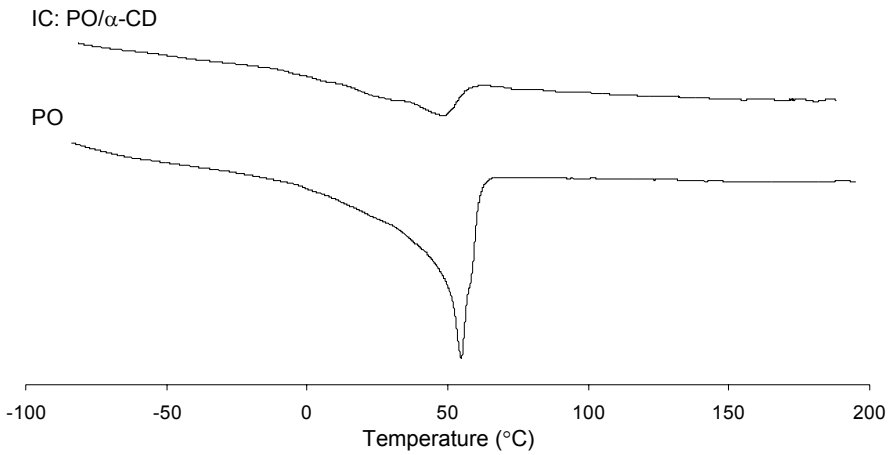

Figure 8.6 – DSC thermograms of PO and α-CD/PO IC showing that not all of the PO was included within the cavities of α-CDs.

On the other hand, a DSC trace of 1,9-decadiene showed a T_m at -64 °C, which was non-existent in the thermogram of the α-CD IC. This led us to believe that the monomer was completely covered by the α-CD and unable to form a continuous phase.

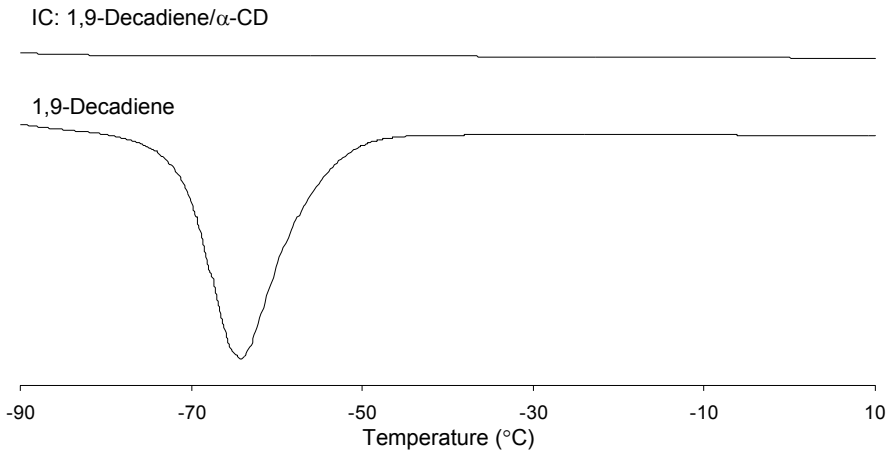

Figure 8.7 – DSC thermograms of 1,9-decadiene and 1,9-decadiene/α-CD IC showing the effect of isolating the monomer units within α-CD cavities; no Tm existed for the IC suggesting the monomer was completely covered by α-CD.

8.3.5 Thermogravimetric Analysis (TGA)

Information from TGA measurements also provided evidence of ICs formed with α-CD.[16-18] When polymer chains were confined within CD channels, an unimodal thermal decomposition behavior was expected, while physical blends usually exhibited two distinct weight-loss transitions corresponding to independent decompositions of the polymer and CD.[15] While this was true for polymers which degrade at temperatures lower than the degradation temperature of the host CD, two weight-loss transitions were observed for ICs formed by polymers that degrade above the degradation temperature of the host CD.[12] The first transition was due to CD degradation, and the second was due to polymer degradation. This was seen in the TGA plot for the PO/α-CD IC in Figure 8.8. The addition of 1,9-decadiene and THF as guest molecules within α-CD did not increase the degradation temperature of α-CD (see Figure 8.9), and suggested that their inclusion did not offer increased thermal stability of α-CD. This was thought to be due to the short length of both 1,9-decadiene and THF when compared to polymers, which could thread through a columnar crystal structure as suggested by WAXD.

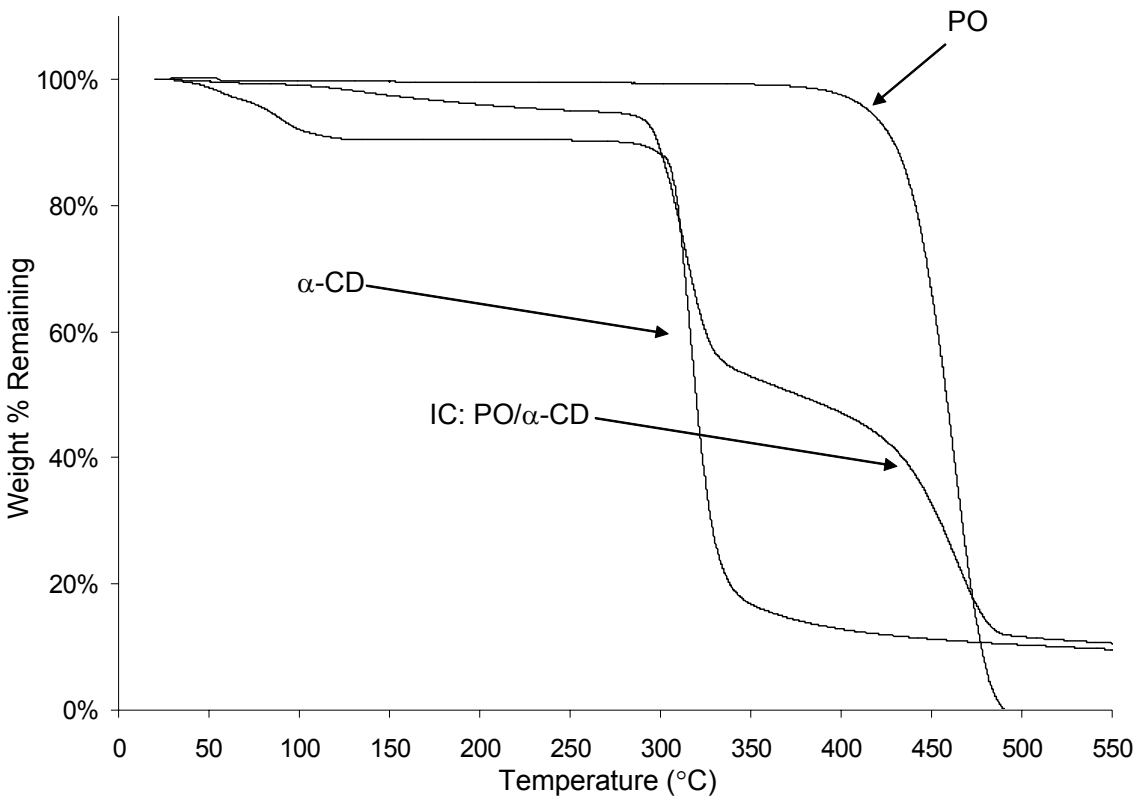

Figure 8.8 – Comparison of thermal degradation behaviors of PO, α-CD, and PO/α-CD IC demonstrated by TGA.

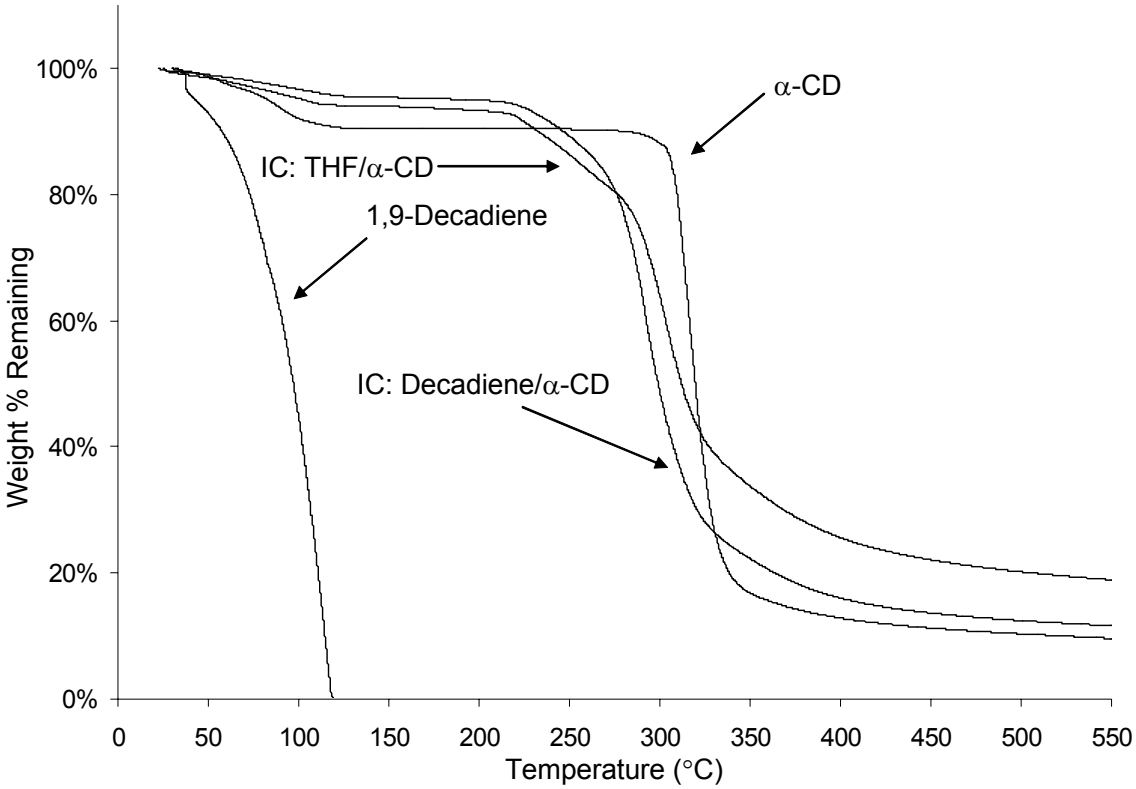

Figure 8.9 – Comparison of thermal degradation behaviors of 1,9-decadiene, α-CD, 1,9-decadiene/α-CD IC, and THF/α-CD IC demonstrated by TGA.

8.3.6 Attempts toward True Rotaxanes

PO/α-CD IC was suspended in a solution of CH_2Cl_2 containing mvBG. Grubbs's 1st generation ruthenium catalyst was added and the mixture was refluxed overnight before being precipitated into methanol. The solid product was not completely soluble in any given solvent, including dimethylsulfoxide, THF, chloroform, and hexane. Therefore, the sample was suspended in hot distilled water and sonicated at 60 °C for 30 min. to dethread and dissolve any α-CD, which was threaded onto chains that were not end-capped. The particulates remaining in the mixture were filtered and found to be completely soluble in CH_2Cl_2. ^{1}H NMR demonstrated that no α-CD was present in this product, which contained only PO and dimerized mvBG.

The 1,9-decadiene/α-CD IC was suspended in a CH_2Cl_2 solution of mvBG. Grubbs's catalyst was added to couple mvBG to both ends of the divinyl monomer. After refluxing for 96 h, the mixture was precipitated into THF and filtered to remove free α-CD; this product was dried under vacuum. Solvent was removed from the filtrate and this solid was examined by ^{1}H NMR, which indicated that no α-CD was present in the sample. As a matter of fact, no peaks representative of 1,9-decadiene were found either.

The solid particles, which were insoluble in THF, are comprised primarily of α-CD, but 1,9-decadiene was also present. No indication of mvBG was present in this ^{1}H NMR spectrum. End-capping an IC of a divinyl compound within an α-CD cavity is difficult for two reasons: (1) the host molecule provides steric hindrance against the bulky catalyst from coordinating to the vinyl group, and (2) if the catalyst is capable of coordinating to the vinyl bond of the guest molecule, the catalyst is in close proximity to α-CD hydroxyl groups that can render the catalyst inactive by coordinating to the metal center.

8.4 CONCLUSIONS

ecPO was unable to form an IC with α-CD, but data suggested that PO, 1,9-decadiene, and THF, were quite capable of forming ICs with α-CD. In the solid-state ^{13}C CP/MAS NMR spectra for the ICs, all $C_{1\text{-}6}$ resonances of α-CD showed less splitting and more unresolved resonances. The peaks at 76.0 and 96.5 ppm, which represent C_4 and C_1 resonances, disappeared in the spectra for the ICs indicating that α-CD adopted a more symmetrical conformation. Diffraction patterns in WAXD for all of the ICs were nearly identical and were similar to previously reported α-CD ICs. DSC suggested that 1,9-

decadiene was completely covered by α-CD because no T_m was present in the thermogram. A T_m was present, however, for PO/α-CD IC, but this T_m was depressed and less pronounced. This suggested that PO was partially, though not completely, threaded by α-CD. TGA demonstrated two degradation temperatures for the PO/α-CD IC; the first was due to CD degradation and the second was due to PO degradation. Only one degradation temperature was observed for ICs formed from 1,9-decadiene and THF.

Two methods are commonly used to prepare CD ICs with polymers. The first is to dissolve the polymer in an organic solvent and add this solution to a saturated solution of CD in water. The disadvantage of this method is that organic solvents have a propensity to become guest molecules within CDs, and the current techniques available to characterize ICs are unable to distinguish between ICs formed from polymers versus ICs formed by solvent. This was demonstrated when THF formed an IC with α-CD and analysis by solid-state ^{13}C CP/MAS NMR and WAXD gave information quite similar to data reported for PEG/α-CD ICs.

ICs of PO/α-CD and 1,9-decadiene/α-CD did not form true rotaxanes by coupling mvBG to the chains ends via ADMET. This chemistry was prevented either by the host molecule blocking access of the catalyst to the vinyl bonds or by the hydroxyl groups of the α-CD molecules coordinating to the ruthenium catalyst.

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CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

9.1 CONCLUSIONS

- ecPO was synthesized via ADMET by polymerizing 1,9-decadiene with Grubbs's 1st generation ruthenium catalyst and utilizing mvBG as a chain stopper. The molecular weight of the polymer was predetermined by the amount of mvBG added to the polymerization.

- According to ^{13}C NMR, the %-*trans* content of ecPO was 84%, and DSC demonstrated a decrease in the expected T_m and T_{cr} temperatures as compared to pure PO.

- PO and 1,9-decadiene formed ICs with α-CD; this was verified when ecPO did not form an IC under identical conditions. The crystalline solids were analyzed by solid-state ^{13}C CP/MAS NMR, which showed that α-CD adopted a more symmetrical conformation as a host molecule. Diffraction patterns in WAXD were nearly identical to previously reported α-CD ICs.

- DSC showed no T_m for the 1,9-decadiene/α-CD IC indicating the monomer unit was completely covered by α-CD. A T_m for the PO/α-CD IC was present, but

depressed in temperature, which suggested that PO was not completely covered by α-CD.

- Two degradation temperatures were observed by TGA for the PO/α-CD IC, which were due to α-CD degradation followed by PO degradation.

- A white crystalline precipitate formed when ecPO was dissolved in THF and then added to an aqueous solution of α-CD. The solid completely dissolved when washed with THF and then washed with water. These results signified ecPO had not been included as a guest molecule within α-CD, but that solvent had played a role in the formation of the precipitate.

- THF was added to a solution of α-CD in water and the solution was sonicated until a white precipitate formed. The product was analyzed by solid-state ^{13}C CP/MAS NMR and WAXD, and the results were similar to data for α-CD ICs with polymers.
- ICs of PO/α-CD and 1,9-decadiene/α-CD did not form true rotaxanes by coupling mvBG to the chains ends with a metathesis catalyst. Coordination of the catalyst to the vinyl end groups was blocked by the CD molecules or the hydroxyl groups poisoned the catalyst by coordinating the ruthenium metal.

9.2 RECOMMENDATIONS FOR FUTURE WORK

- DSC of the PO/α-CD IC demonstrated a T_m, which indicated crystallinity within the sample, presumably, because PO was not completely covered by the host molecules. WAXD, however, did not show a diffraction pattern indicative of PO crystallinity. WAXD measurements were taken several days before DSC data was collected, and the T_g of PO is below room temperature, so crystallization may have occurred in the time between the two analyses were taken. These results should be further investigated by measuring crystallinity of PO/α-CD ICs as a function of time.

- Synthesizing true rotaxanes directly from α-CD ICs with PO and 1,9-decadiene was not accomplished, but ADMET can be utilized to prepare a variety of telechelic polymers that can be end-blocked after an IC is formed. Tosylated-9-decenol can terminate ADMET polymerizations of 1,9-decadiene. This telechelic polymer can form an IC with α-CD, and then the polymer can be end-capped by a literature procedure.[1]

9.3 REFERENCES

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VITA

Bryan M. White was born in Morrilton, AR, on January 25, 1977, but he and his family moved to Wynne, AR, shortly thereafter. Bryan attended Wynne High School during his freshman and sophomore years where he excelled in football, baseball, and track. In the summer of his junior year, he transferred to the Arkansas School for Mathematics and Science in Hot Springs, AR, and was a member of the charter class, which graduated in May 1995.

In the fall of that year, Bryan attended college at the University of Tulsa in Tulsa, OK. He worked under the direction of Dr. John C. DiCesare synthesizing sulfur-containing organic compounds until his graduation in May 1999 with a Bachelor of Science degree in Chemistry.

In August 1999, Bryan and his new wife moved to Atlanta, GA, where he began work toward a Ph.D. in Chemistry at the Georgia Institute of Technology. He worked for Dr. Haskell Beckham until his graduation in May 2004.